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Recovery of Sugars From Cane Molasses by Continuous Simulated Moving Bed Ion-Exclusion Chromatography.

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RECOVERY OF SUGARS FROM CANE MOLASSES BY CONTINUOUS SIMULATED MOVING BED ION-EXCLUSION CHROMATOGRAPHY

A Dissertation

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by
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ABSTRACT

Present investigation was undertaken to determine the feasibility of using a Simulated Moving Bed (SMB) Ion Exclusion Chromatographic system for the recovery of sugars from molasses. The recovery of sugars from molasses is complicated because of the presence of high concentration of salts of K, Ca, Mg, etc. The presence of these salts in the molasses prevents sucrose to crystallize. SMB Ion Exclusion Chromatography has been shown to be successful to recover sugars from beet molasses, and to separate sugars from each other in High Fructose Corn Syrup industry. The basis of the ion exclusion is that the sorbent used in the column prevents the salts from being adsorbed whereas the sugars are adsorbed on the resin. The adsorbed sugars in the resin are recovered by elution with water. The efficiency of the SMB Ion Exclusion system for separation of sugar and non-sugars is affected by variables such as concentration of ionic material in the molasses, flow rates in different zones of the system, concentration of the molasses etc. In the first phase, equilibria and kinetics of the system were studied for proper modelling and design of the SMB operation. In the second phase, properly treated cane molasses were used as feed for SMB pilot plant with parameters obtained from "best" simulation data. Two products, Extract (high sugars; low non-sugars) and

Raffinate (high non-sugars; low sugars) were obtained. The quality of the extract is very promising for recovery of sucrose in crystalline form as it contained 81% sucrose, (96% total sugars) and only 4% non-sugars. The raffinate, with 36% total sugars, still has enough caloric value to be used as cattle feed. SMB recovery of 88% sucrose (80% in crystalline form) and 79% of total sugars achieved warrants a potential increase in total recovery of sucrose by 11%.

Chapter 1

INTRODUCTION

Sucrose, the "sugar" of everyday life, is a pure natural nutrient. The sweetness of sugar has long been a preferred means of improving acceptability of foods. Sugar provides not only sweetness, but it is also responsible for valuable functions including structure, mouth feel, texture, and flavor enhancement. About 65 % of world sugar production is derived from sugarcane, the rest comes from sugarbeet (World Sugar News, 1990).

Standard sugar processing for cane and beet (Clarke, 1990) involves extraction of juices, clarification to remove non sugar material and concentration by evaporation to syrup. Sugar is recovered from the syrup by repeated crystallization. Final molasses is a heavy, viscous liquid separated from the final low-grade massecuite from which no more sucrose can be crystallized. This is because of the practical limit has been reached due to kinetics of crystallization. Recovery of sucrose is not economically viable from final molasses by conventional procedures. The sum of the sugars (sucrose and invert) generally constitutes at least 50-55 % of the final molasses (Saska, 1988). This results in a loss of about $50,000 every day for a mill processing 10,000 tons of cane per day, at present market price of sugar.

The recovery of sugars from molasses has been the objective of many researchers. Various methods, which include lime precipitation, adsorption, ion-exchange, solvent extraction, and conversion of sucrose to invert, have been attempted to recover sugars from cane molasses. However these methods have limitation that restrict their commercial applications.

Liquid chromatography in its various forms has acquired an important role in a variety of industrial applications in recent years. Though the use of chromatography for analytical purposes has been known for some time, the industrial scale uses have been much more limited until recently. Because of the importance of chromatography in analytical and industrial applications, this subject has been studied so extensively that Journals have bee dedicated to chromatography. Advances in liquid chromatography, such as improvement in ion exchange engineering, better resin characteristics and control methods have resulted in effective preparative and production scale separations (Herve and Lancrenon, 1989).

Commercial application of chromatography, as a separation technique in the petrochemical, pharmaceutical and food industry, prompted scientists to explore its potential applications in the sugar industry. Innovation in liquid chromatography documented the application of ion

exclusion as a unit operation for the separation of ionic components from non ionic components over a bed of ion exchange resin, by Dow Chemical Co. in 1953 (Wheaton and Bauman, 1953). Combination of Simulated Moving Bed (SMB) technique with Ion Exclusion chromatographic system was a new development in continuous chromatography (Broughton, 1968). It is a method of (continuous) countercurrent chromatography that avoids the difficulties of moving solid media. It leads to reduced solid media inventory with higher efficiency of the system (Kearney, 1990).

SMB Ion Exclusion allows separation of various sugars and non sugars from process streams such as molasses. This process is successful for separating sugars from beet molasses (Chertudi, 1991; Herve and Lancrenon, 1989; Gadomski, 1991; Hongisto, 1979), but could not be applied to cane molasses until very recently, because of intrinsic differences. Beet molasses contains about 20% more sucrose, negligible inverts, and 10-15 times less hardness than cane molasses (Schneider, 1978).

Chromatographic separation requires a clean feed free of any suspended material. Bivalent cationic components must be minimized to avoid any ion exchange during the separation which can impair the efficiency of the system (Aguirre, 1982).

Economic pressure from the alternate sweetener industry has prompted the scientists to look for the application of

SMB Ion Exclusion technique for recovery of sugars from cane molasses.

The purpose of this study was to investigate the feasibility of recovery of sugars from cane-molasses by SMB continuous ion exclusion process. The sorbents to be used as solid media in this study have to be characterized followed by experiments on pre-treated cane molasses on a scalable pilot plant. At present the type of system limits study to sulphonated polystyrene materials.

Chapter 2

LITERATURE REVIEW

2.1 Introduction.

Crystallization is the most important of the sugar recovery processes. Sucrose is transformed into crystals by repeated crystallization. Crystals are then separated in centrifuges from the mother liquor- molasses. The recovery of further sucrose is not economically practical by standard crystallization procedures and the residual molasses is called final molasses. This contains about 8-15% of the sucrose introduced at the mill house (PSST, 1989; Schneider, 1978). The compositions of final molasses of beet and cane are given in Table 1.

Table 1:
Average composition of cane and beet molasses.
(on 100% dry solids)
Mainly from: Saska (1988) and Schneider (1978)

Components	Cane Molasses	Beet Molasses
Sugars	58.5	64.5
Sucrose	45.5	64.0
Reducing Sugars	13.0	0.5
Glucose	5.0	0.3
Fructose	8.0	0.2
Other Reducing Compounds	1.5	xxx
Ash	15.0	12.5
Others (org/inorg non-sugars)	25.0	23.0
Colorants	2.3×10^5 I.U.	7×10^4 I.U.

Considering total sugars in molasses (at least 50 %), their market value is equivalent to about $0.05 per pound of sucrose compared with $0.23 for raw sugar at current molasses prices (Clarke, 1990; Kearney 1990). As a base case for 1,000,000 tons of cane brought to the mills, this loss is about $4.7 million (King, 1991).

Interest in recovery of sugars from the molasses is not new. Many attempts have been made to recover sugar from molasses but without commercial success. For a successful separation, the advantage can be taken of difference in behavior of sucrose compared to the other components of the molasses including polysaccharide, invert and inorganic and organic non sugars. This difference can be either chemical or physical. The illustrative reaction of sucrose with calcium leads to the formation of insoluble complexes of calcium saccharate. The precipitated complex is treated in water with carbon dioxide to give sucrose and insoluble calcium carbonate. This is the basic principle of the Steffen process (Hartmann, 1982). The Steffen process is employed under some circumstances in the beet industry. It does not work for cane molasses. This is because of intrinsic differences of the molasses, mainly less sucrose and higher concentration of salts in the cane molasses. (Table 1).

A physical property that has been used to recover sucrose is solubility difference of sucrose in solvents.

Liquid ammonia, ethanol and a mixture which includes benzene have been tried (Reich, 1948; Othmer, 1978). Though some hold promise as means of pre-treatment for further processing, none have been commercially applied. Potential health hazard and high cost of solvents recovery have made this alternative unattractive.

A very high quality product, in terms of clarity and palatability, can be obtained by filtration of molasses through very fine membrane (< 1 μ). But as this does not separate sugars from ash and non sugars, it is of no importance as a direct means for sugar recovery (Scott 1986). Rather with membrane filtration, a clean feed can be obtained for chromatographic system. This will help to avoid any potential problem of filling up the voids of the system with suspended materials and colloids.

Electrodialysis, involves the selective removal of ions through a membrane under the influence of an electric field. This technique is being tried in Japan and Indonesia to improve molasses exhaustion and for better fermentability (Masaki and Kokubu, 1986; Anon., 1982).

Chromatographic separation processes have been applied in the beet sugar industry (Landi and Mantovani, 1975; Lancrenon and Herve, 1988). The beet-sugar industry had realized the importance of ion-exchange technology as a means of improvement of sugar yield, quality, and elimination of constituents causing process difficulties.

Ion-exchange technology has been used in the beet sugar industry:

- to remove Ca and Mg from second carbonation juice to avoid incrustation in the evaporator.
- to remove ionic non-sugars, cations and anions, from juices or syrups to increase sugar yield.
- to replace one ionic species with another one of less melassigenic power to achieve higher molasses exhaustion leading to an increased crystalizable sugar fraction.
- to remove coloring material from process sugar solutions,to have a better quality crystallized sugar.
- liquid sugar production from thick juice.

2.2 Adsorption/Ion Exclusion.

Adsorption is a separation process by which the solutes of a solution are selectively removed and adsorbed by a solid adsorbent. A solid sorbent is held in a fixed bed, and a fluid is passed continuously through the bed until the sorbent is nearly saturated and desired separation can no longer be achieved. The fluid flow is stopped and the adsorbent is washed with an eluent. The solutes are thus removed out of the fixed bed with the eluent (Wankat, 1986). This process is based on the ability of certain solids of preferentially concentrating on their surface specific substances from the solution in contact. When a mixture of solutes comes into contact with a solid adsorbent, the first

component to emerge with eluent will be the least adsorbed, the strongly adsorbed component will be eluted last.

Interaction of solutes with the solids sorbent may be described by physical adsorption, or chemisorption.

Physical adsorption, results from van der Waal's forces of attraction between molecules and sorbent. This attraction is a result of asymmetrical charge on the molecules of solutes. Van der Walls forces comprise of London forces and classical electrostatic forces (Ruthven, 1984).

Chemisorption results by the chemical interaction of solute and sorbent. The forces involved in this type of adsorption are stronger compared to physical adsorption, thus usually this is considered an irreversible process.

The basis of the "Ion Exclusion" process is that ionic and non-ionic solutes can be separated on a bed of high charge density solid material, such as ion exchange resin. Ion exchange resins on contact with an aqueous solution absorbs water into the beads (Fritz, 1987). This is attributed to the presence of highly polar functional groups. The functional groups can be sulfonate for a cationic resin and quaternary ammonium for an anionic resin. Microporous resins when hydrated, swell and form a gel like structure. Upon dehydration, these resins shrink. Fig. 1 explains the main features of a cation exchange resin.

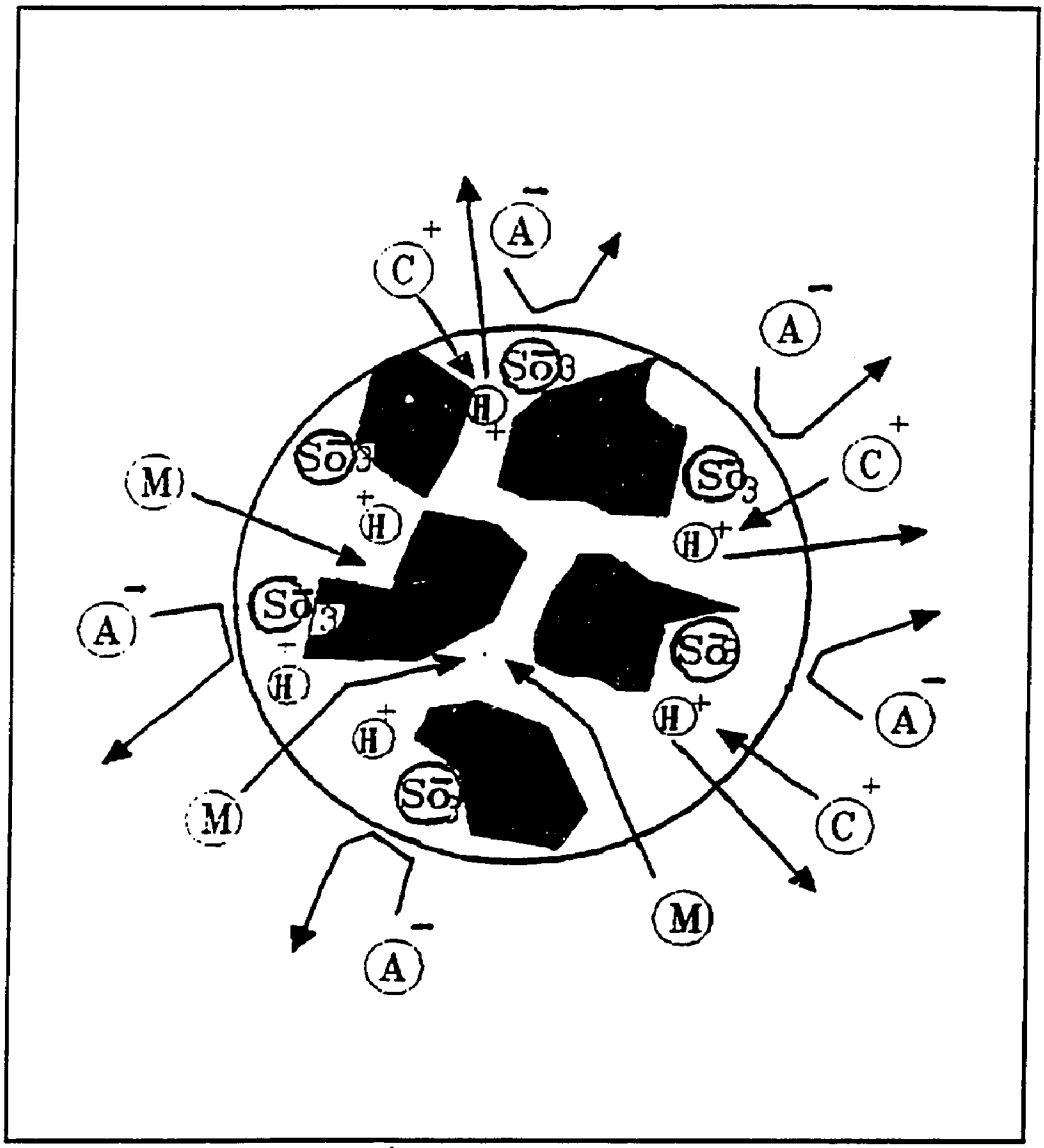

Figure 1: Schematic representation of cation exchange of C^+ and H^+ ions, exclusion of anions A^-, and free movement of neutral molecule M. (After Fritz, 1987)

The sulfonic acid $-(SO_3)^-$ groups are attached covalently to the benzene ring of the polymer, and their movement is severely restricted. However, the counter ions are electrostatically attached to negative sulfonate groups, Hydrogen in this case, and are free to move about in the water filled pores and channels inside the resin.

Ion exchange occurs when an ion from the outside solution enters the resin, and an ion leaves the resin. This exchange is effective even well inside the resin. In case of a cation with 2^+ charges, two ions have to leave the resin for each cation, to preserve electro-neutrality.

Ion-exclusion takes place when the barrier of fixed SO_3^- groups prevent the anions from the outside solution to enter the resin, and thus anions of the solution are repelled by SO_3^- group of the resin.

The ion exclusion process is a combination of two different phenomena taking place on the same ion exchange resin simultaneously: Electrolytic exclusion due to the Donnan Equilibrium, and Adsorption.

2.2.1 Donnan Membrane Effect.

According to the Donnan membrane theory, ions in solution tend to be repelled from an ion exchange resin by alike ions occupying the resin's ion exchange sites.

Friedrich (1962) has reviewed the Donnan Equilibrium in detail in "Ion Exchange". A cationic exchange resin contains fixed anions and is capable of exchange cations.

When a cation exchange resin, which contains no sorbed electrolytes, comes in contact with a dilute solution of a strong electrolyte there is a considerable concentration difference between the two phases. The cation concentration is higher in the resin, while the anion concentration will be higher in the solution. Because of this concentration difference, a diffusion of both, cations to solution and anions to the resin will, take place. By this diffusion electroneutrality will be disturbed, as the migrating ions are charged, resulting an accumulation of positive and negative charge on solution and resin, respectively. Thus an electric potential difference between the two phases will build up. Because of this potential, cations are attracted back to the resin, and anions will be attracted back to the solution. By the action of the electric field, a tendency of ions to level out the concentration difference between the both phases will be balanced and an equilibrium will be established. The immediate consequence of this equilibrium is that electrolytes are excluded by the resin. These electrolytes will tend to pass through the void volume of the column of resin rather than through the resin itself, thus will have a shorter pathway than non-electrolytes which pass through the pores of the resin beads. It has been reported that the Donnan effect does not totally excludes electrolytes from the resin but merely induce a tendency for the electrolytes to pass around the resin beads.

Donnan effect is enhanced by low concentrations of electrolytes in solution and high capacity and cross linkage of the resin. A high capacity or high cross linkage resin has higher internal (molal) counter-ion concentration.

Donnan effect is suppressed partially or negated by association, complex formation or similar interactions between the electrolytes and the fixed ionic groups and also by association of mobile ions by themselves.

2.2.2 Sorption Equilibria.

Sorption equilibria are basis for determining the behavior of an ion exclusion system (Vassiliou and Dranoff, 1962). The system's performance is dominated by the way in which equilibrium varies with rising solute concentration in fluid phase as equilibria have strong influence on the mass transfer driving force. Sorption equilibria are frequently described by adsorption isotherms and distribution coefficients.

Adsorption Isotherm.

Adsorption isotherm is a single curve which represents the equilibrium relationship between the concentration in solid resin and concentration in external solution at a given temperature. A particular set of conditions such as solution concentration, ionic form of resin, etc. corresponds to one point on the isotherm.

Different types of adsorption isotherms have been discussed in the literature. These have been broadly

classified as linear and non-linear by Brunauer and coworkers (Perry 1989). Non-linear isotherms are further classified as Favorable; Unfavorable; and Irreversible (Fig 2).

A linear isotherm is the simplest one describing the solid phase concentration as a function of the fluid phase concentration. It is easier to treat theoretical models based on the assumption of linear adsorption, but it is not always the case, so care should be taken while developing parameters for separation, as it would lead to less than optimum efficiency of the system (Saska et al., 1991)

Under some conditions, for example an increase in concentration, solutes behave in a different way, either they favor the solid or the fluid phase. If adsorbent has greater affinity at lower concentration relative to affinity at higher concentration for a solute, it will result in a favorable isotherm, but if the case is reversed, then the resulting isotherm will be unfavorable. The convex upward shaped isotherms are called favorable because relatively high solid loading can be obtained at a low concentration in the fluid. The concave downward shaped isotherms are called unfavorable. In this case, relatively low solid loadings are obtained and thus it leads to quite long mass transfer zones in the bed.

Irreversible isotherms are a limiting case of very favorable isotherms. Irreversible isotherms arise from a

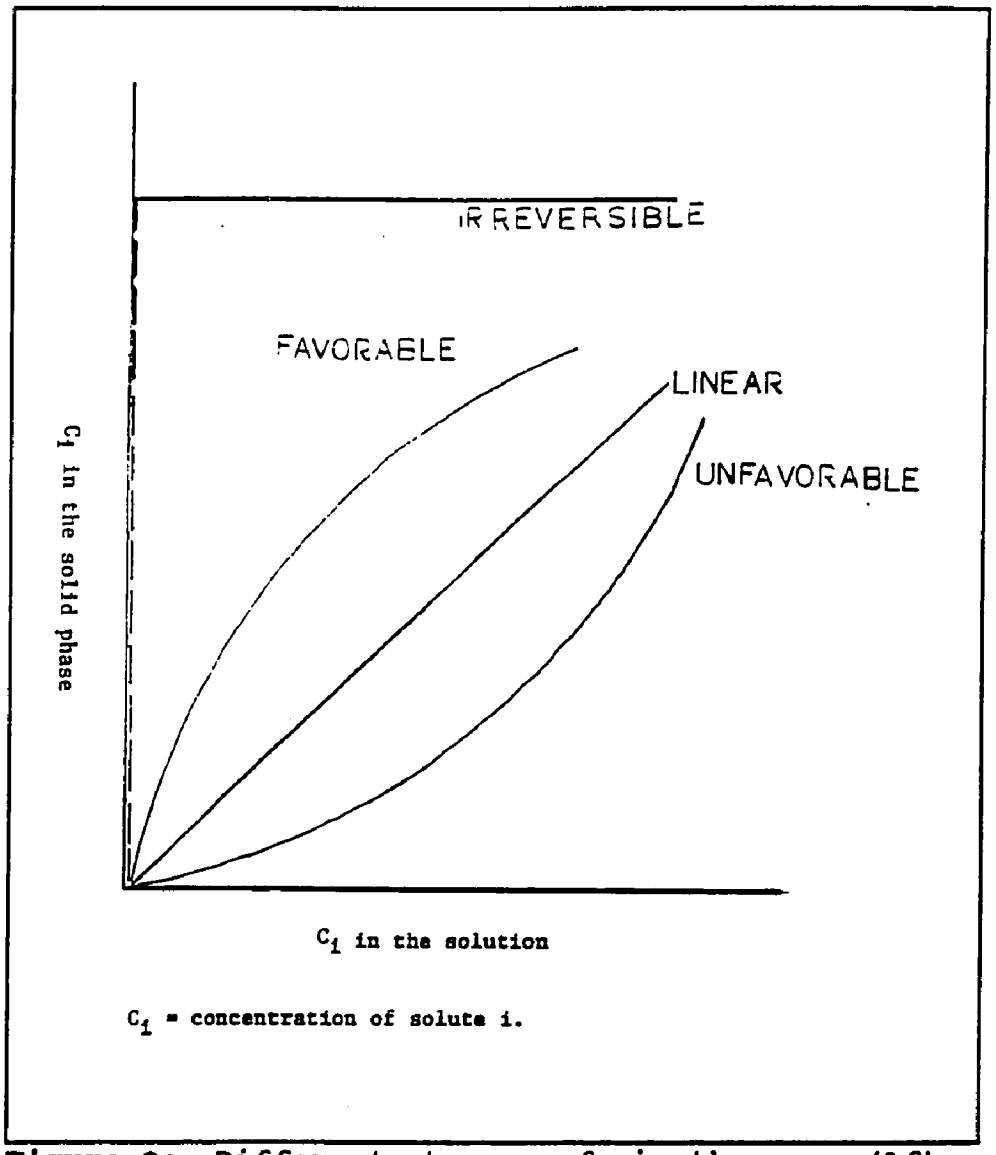

Figure 2: Different types of isotherms. (After Aguirre, 1982)

strong adsorbent-solute interaction. The solute is picked up from the solution till the saturation on solid phase is reached, and then adsorption process is ceased irrespective of any change in the fluid concentration.

Distribution Coefficient.

Distribution coefficient K, of a solute, is the ratio of concentrations of the solute in the solid phase and in the solution.

$$K = \frac{C_i \text{ in the solid phase}}{C_i \text{ in the solution}}$$

Where C_i is concentration of solute i.

Distribution coefficients are in conformity with one point on the adsorption isotherm, describing the ratio of the ordinate value to the abscissa value at this particular point. In case of linear isotherm, the distribution coefficient is independent of concentration. Retention time of different components in the column is related to the distribution coefficient. The higher the value of K, the more the component is retained by the adsorbent.

2.3 Design of Adsorption/Ion Exclusion System.

2.3.1 Fixed Bed Chromatography.

The general principle of chromatographic separation is the introduction of (a batch) of mixture of components to be separated onto a chromatographic column (Fig. 3). A mixture of A+B is fed to the column. Then eluent W, is introduced from the top. While passing through the column under the

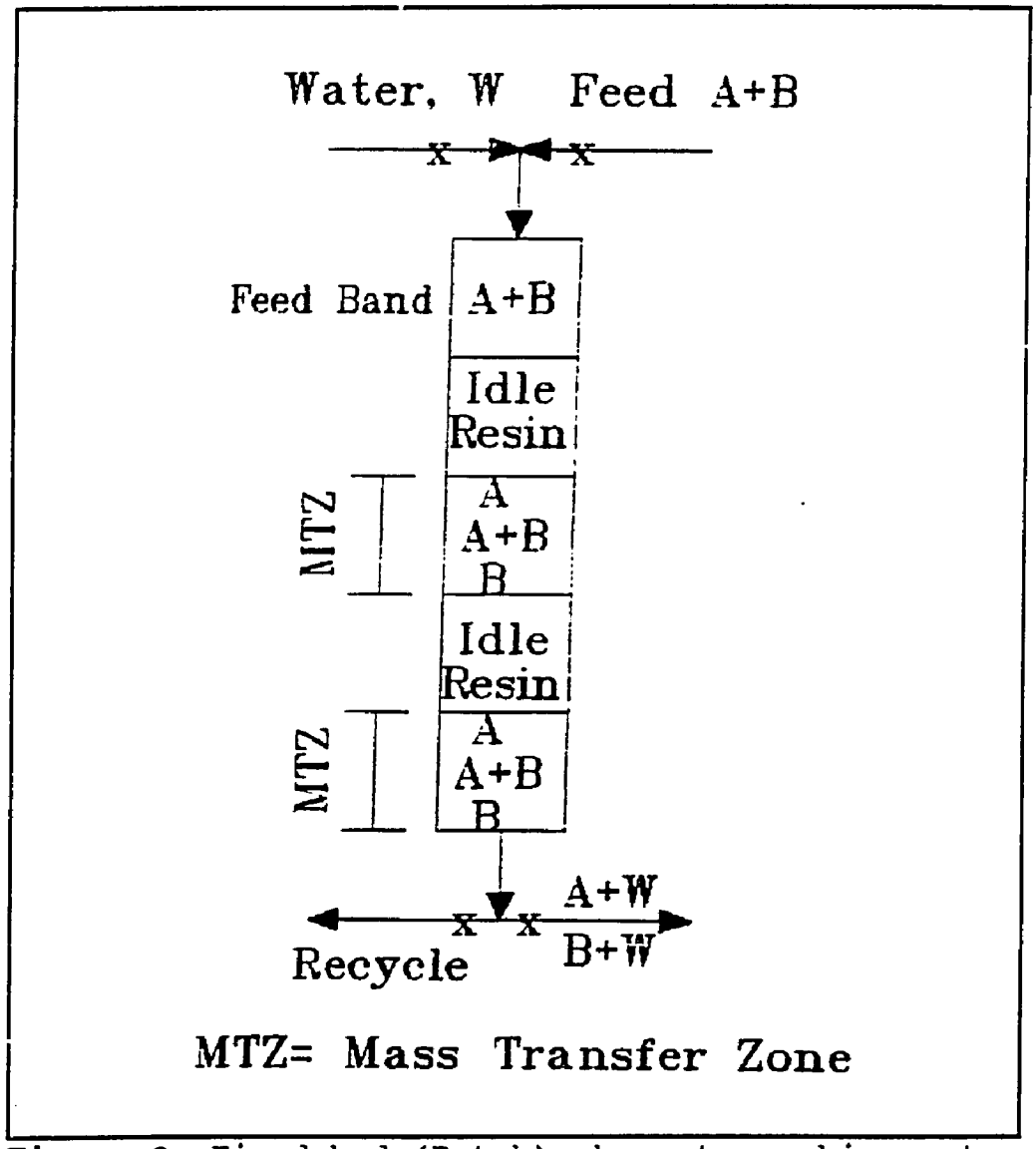

Figure 3: Fixed bed (Batch) chromatographic system for the separation of A and B components of a mixture with water as eluent.

influence of eluent flow, mixture (A+B) is separated into its components A and B which are collected at the column exit at different timings. Between the separated components there is still a mixture of A+B components which is recovered and recycled in order to maximize the recovery of components. After a batch of feed is introduced and elution is started, some time is required to wait for next batch of feed to be introduced. This leads to an unutilized resin shown as idle resin. This is not a continuous process from the standpoint of feed introduction and product extraction.

Normally on preparative scale, the columns are overloaded to achieve maximum production of desired component. It is done at the cost of separation efficiency, as for any chromatographic system for practical purpose, there is always a compromise between separation and capacity. Extensive recycling, necessary to have maximum recovery, is another drawback of this system. It gives a high purity product and increased overall recovery, but the recovered product stream is very diluted, increasing downstream concentration costs. Inefficient utilization of separation media is a problem associated with fixed bed system. The media actually involved in separation is contained only in those regions of the column where mixtures of components are (Fig.3). With the travel of feed pulse downward through the column, the amount of media actually involved in separation is decreased. Despite the use of

repeated sample injections and recycling, the batch process tended to have restricted column utilization and consequently limited throughput (Morgart and Graaskamp, 1988).

2.3.2 Moving Bed System.

The moving bed system was developed to overcome the problems of a fixed bed system. It is designed to improve efficiency of separation and operate continuously. In this system, solid media is moved countercurrent to the fluid, (Fig.4). The total packed height will equal the mass transfer zone (MTZ), compared to two to three times the MTZ in case of fixed bed system.

In countercurrent chromatography, a liquid phase is made to travel in an opposite direction to a solid phase (Barker and Chuah, 1981). This may be performed in three ways, namely by a moving bed, a moving column, and moving ports co-current to the flow of the mobile phase. Countercurrent action is very important to maintain a constant driving force for mass transfer.

In continuous chromatography, effective use of the bed length has increased. This leads to higher efficiency of the system and reduction in solid inventory. Concentrated streams of product save energy for downstream treatment. Continuous units are smaller than fixed bed units and require less sorbent. In this system, feed (A+B) is introduced in the middle of a vertical column, the solid

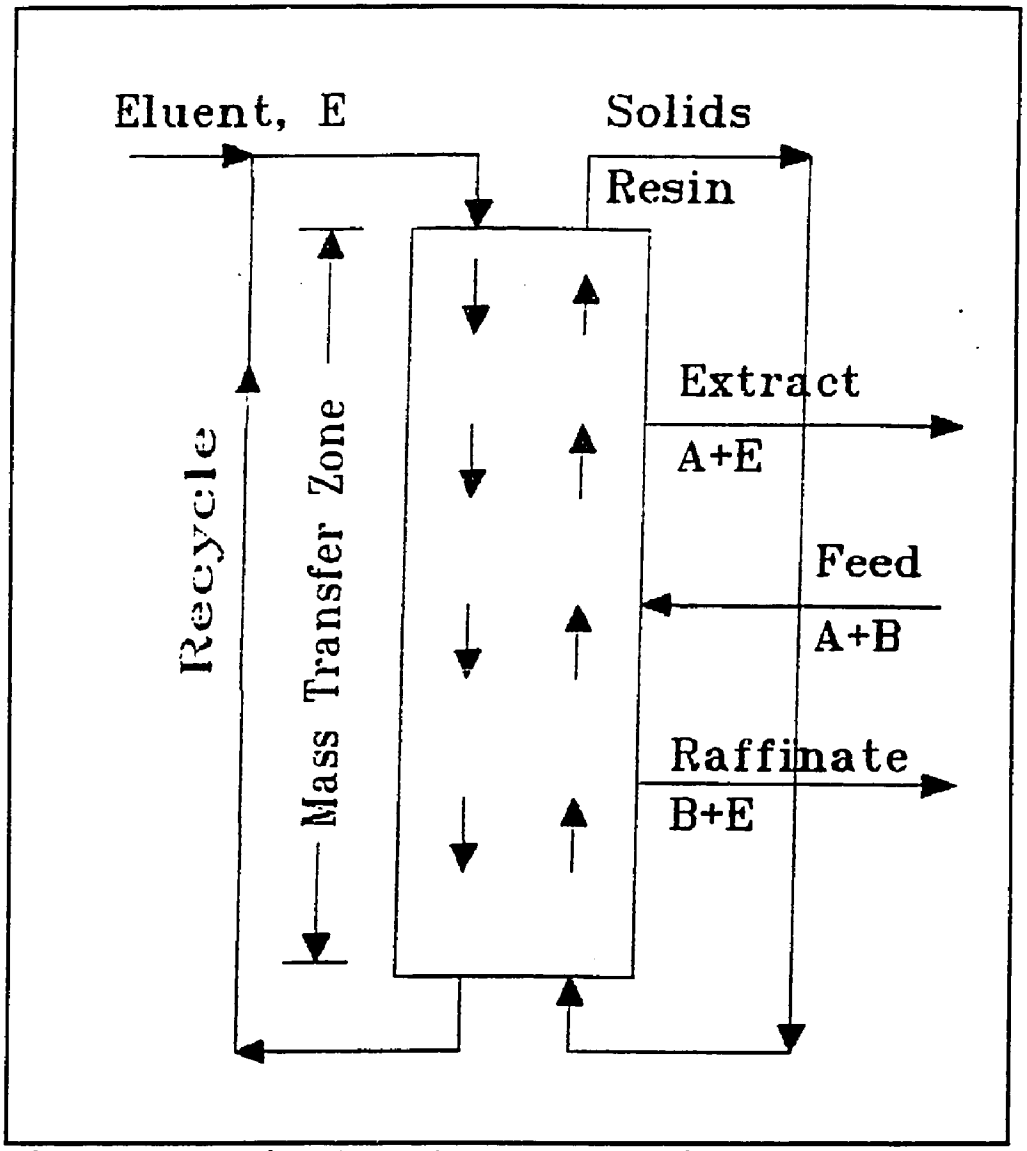

Figure 4: Moving bed chromatographic system for the separation of components A and B with an eluent E. Resin is moved counter to liquid by mechanical means.

media is moved upward by mechanical means. (Fig.4) Component with greater affinity (A) for sorbent, will move upward with solid media, while the other component (B) will move downward. An eluent (E) is introduced above the feed inlet, it will desorb the media as it moves upward. A product (A+E) stream will be obtained between feed inlet and eluent inlet. Similarly, another product (B+E) will be extracted below the feed inlet. The process can be run continuously producing two separate components streams. Countercurrent motion of the solid and the fluid with minimum axial mixing is achieved by:

1) Solid flows opposite to liquid flows, or,

2) Holding the solid rigidly and moving the equipment (e.g. resin is held on a belt and the belt is moved through the system).

This system requires complex mechanism to move the media around the system. Physical attrition of the resin is a serious problem. To maintain plug flow is difficult at the same time. That is why that no matter that theoretically the idea is very sound, but practically, it is very costly.

2.3.3 Simulated Moving Bed (SMB) System.

Simulated moving bed system is a modified version of fixed bed chromatographic separation process. The basic idea of SMB system is illustrated in Fig. 5. A fixed bed chromatographic column is divided into discrete sections by

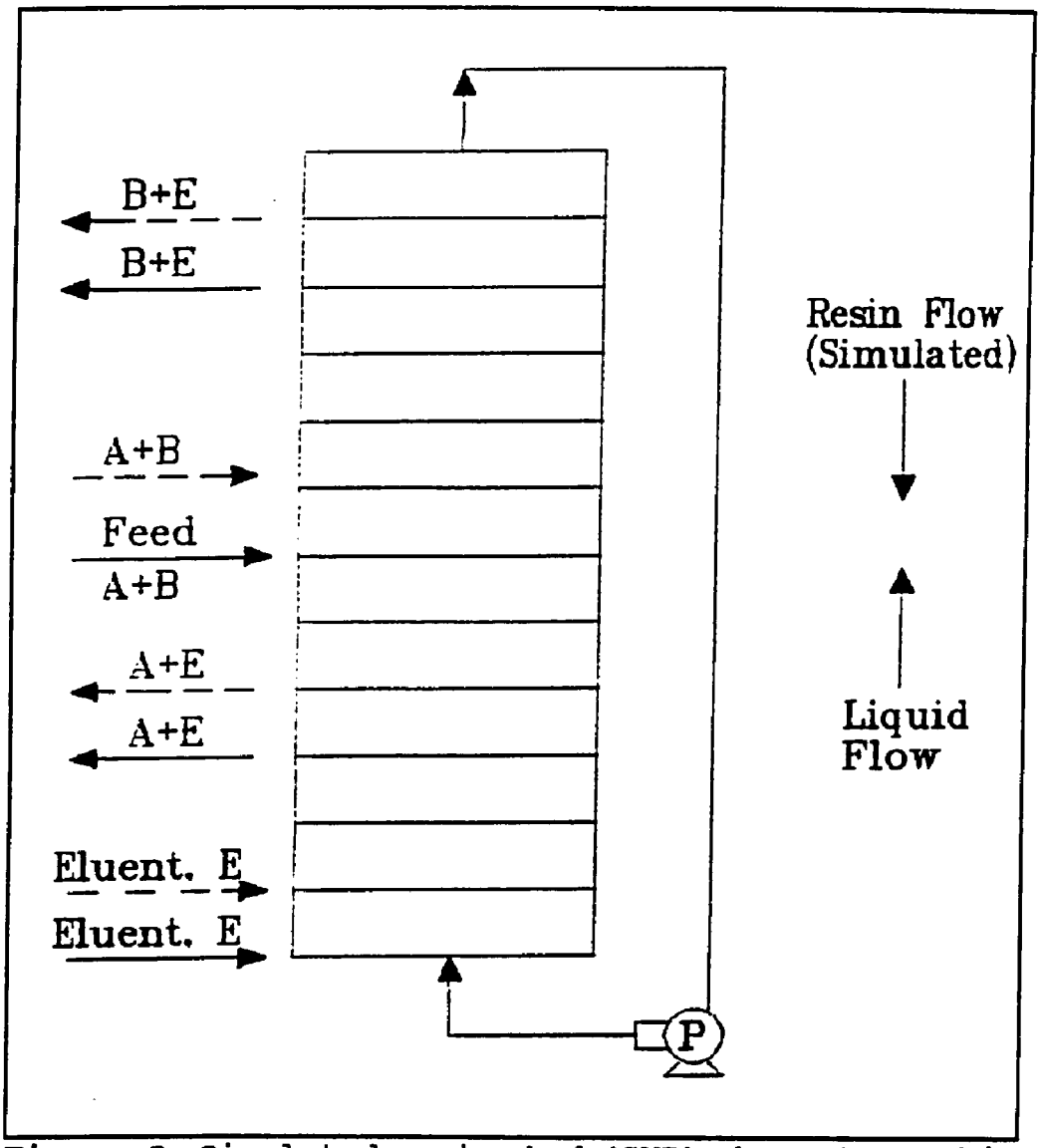

Figure 5: Simulated moving bed (SMB) chromatographic system. A countercurrent simulated flow of resin is achieved by moving process streams in the direction of fluid flow.

distributors which allow the fluid in and out of these sections. An arrangement is made to deliver the feed and eluent to the appropriate section of the column, and extraction of products and recycling simultaneously. After a certain time, the feeding and extraction points are moved to the next downward section of the column and so on. By proper selection of flow rates and switching time, a steady-state profile can be maintained while continuously introducing feed and extracting product streams (Broughton et al., 1970; Morgart and Graaskamp, 1988). Flow rates and switch times have to be considered of in determining the net solution flow. The net solution flow equals the liquid flow less the simulated counter current flow which occurs when the valves sequence one section forward. The column sections are divided into four zones, based on the position of the external streams. (Fig. 6) Each of these zones perform a different function (Wankat, 1986; Broughton et al., 1970; Broughton, 1968). Component A of the feed is considered highly adsorbed on the resin compared to component B.

Zone I: Adsorption zone. In this zone component A is separated completely from the rising liquid stream. When entering this zone, solid contains component B and E already adsorbed onto it. Component A is picked up from the liquid and gets adsorbed on descending solid. A stream of components B and E is produced, which is withdrawn from the

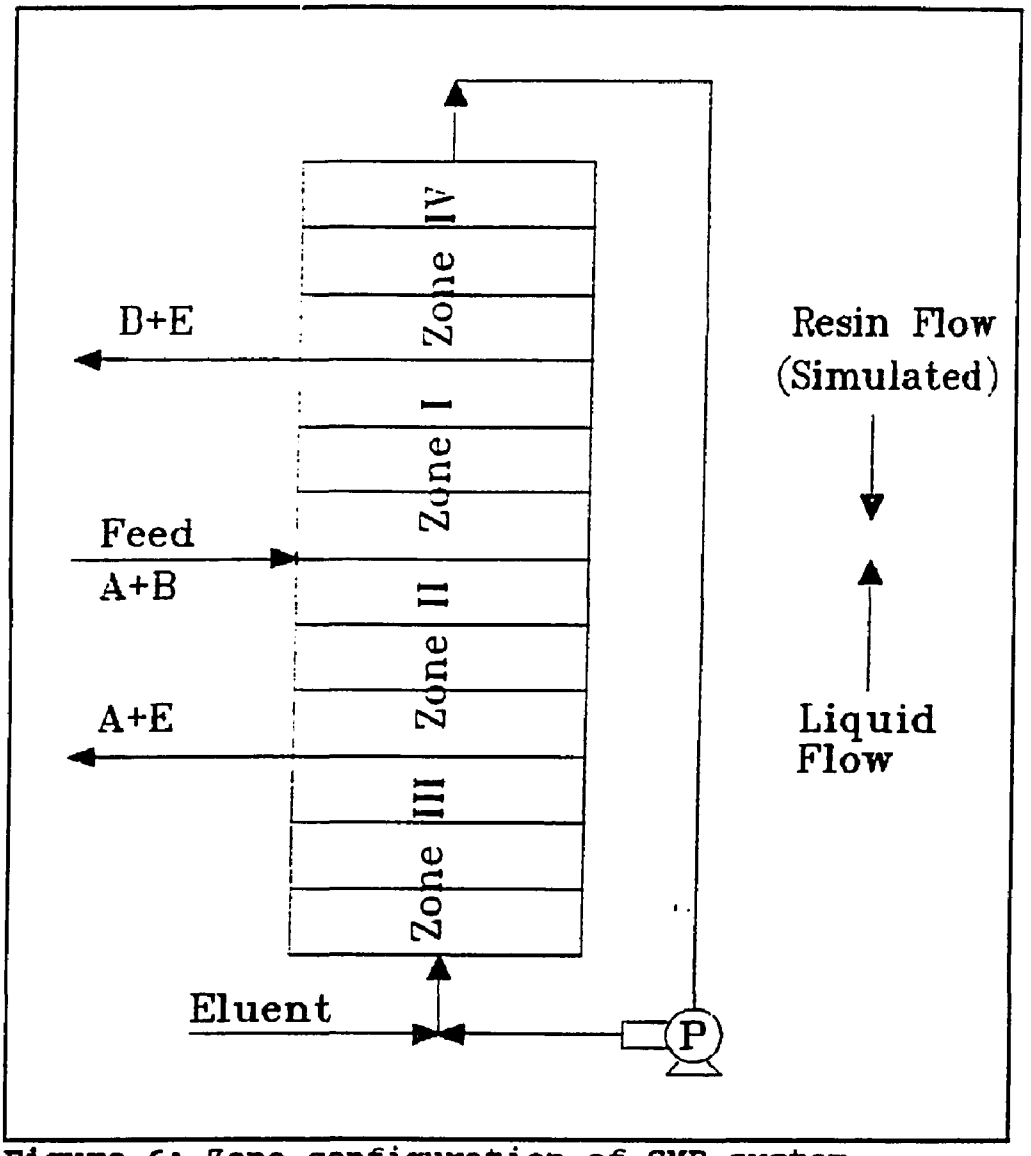

Figure 6: Zone configuration of SMB system.

top of this zone. Component A partially replaces eluent E on the solid.

Zone II: Desorption of Component B. In this zone, component B is completely removed from the solids. Since solid has just come in contact with fresh feed so it carries components A & B simultaneously while entering this zone. The component B is gradually desorbed from the solid by the liquid entering the bottom of the zone which already contained component A and eluent E. Because of greater affinity of component A for the solid than component B, so it becomes possible to accomplish the complete removal of component B without removing all of the adsorbed component A from the solid.

Zone III : Desorption Zone. In this zone component A is completely desorbed from the solid. Solid carries component A along with eluent E adsorbed onto it when enters this zone. While the liquid entering from the bottom of this zone contains only eluent E, component A is gradually desorbed by eluent while solid descends. Component A is then removed from the system at the top of this zone.

Zone IV : Partial Recovery of Eluent E. When solution enters this zone, it contains component B and eluent E. The eluent E is recovered by partial adsorption of B on resin and the eluent is sent to Zone III, where it serves as desorbent (Fig. 6). Thus it helps to reduce the use of fresh desorbent.

To have optimum separation between A and B in the above case, it is necessary that B should move faster than the port movement in Zone I and Zone II and move slower in Zone IV, such that B is moving up in Zones I and II and down in Zone IV,

$$U_{port} = 1_{port} / t_{port} = V_{solid}$$

where U_{port} = Average velocity of port.

1_{port} = Length of bed between ports.

t_{port} = Time for movement of one port to the next stream point.

V_{solid} = Solid (resin) velocity.

To have conditions to get A at exit in the A product, the flow should be such that

$$U_{A1} , U_{A2} > U_{port} > U_{A4}$$

where U_{A1}, U_{A2} and U_{A4} are the velocities of component A in zones 1, 2 and 4, respectively.

In fact, $U_{A1} > U_{A2}$ that is speed of A in zone I will be faster than in Zone II, since the fluid velocity will be greater in Zone I.

To get B at exit port in B product, B should move downward in Zone I and II and upward in Zone III. This should be possible only if

$$U_{B3} > U_{port} > U_{B1} , U_{B2}$$

where U_{B1} , U_{B2} and U_{B3} are the velocities of component B in zones 1, 2 and 3, respectively.

The above mentioned assumptions are the basis of designing of a SMB continuous operation. SMB Ion Exclusion system is flexible, by adjusting different parameters, for example, switch time, flow rates of input or output, and/or the number of sections per zone, products of choice can be obtained. The separation profiles for desired purity and recovery can be modified to suit the conditions of the separation. Simulated moving bed technique offers all the advantages of continuous process without actual movement of resin. These includes a higehr efficiency, reduction in solid inventory by a factor of 25, desorbent circulation is reduced to half the batch system as shown in Table 2. (Broughton et al., 1970).

Table 2:
Comparison of adsorbent and desorbent requirements for the extraction of p-xylene @98.5% recovery and 99.5% purity. From Broughton et al. (1970).
a. For batch system:

Number of HETP, N_B	**263**
Liquid Rate, Ft^3/hr	**400**
Bed Volume, Ft^3	**20,600**
Desorbent/Feed Ratio (D/F)	**3.0**

b. For simulated moving bed system: (D/F = 1.44)

Zone	Number of HETP, N_B	Liquid Rate, ft^3/hr	Adsorbent Inventory ft^3 , (Bed Volume)
I	20	181.2	158
II	25	81.2	252
III	25	218.0	232
IV	20	74.0	162
Total	90	----	804

2.4 Industrial Separation of Sugars.

Use of ion exchange material with simulated moving bed (SMB) technique proved to be commercially successful for the fractionation of different organic compounds with similar distillation characteristics, such as mixtures of aliphatic and aromatic hydrocarbons. In 1978, Ion Exclusion Simulated moving bed (SMB) was used to fractionate fructose from glucose in aqueous solutions. A Zeolite adsorbent was used by UOP, Inc. for separation of dextrose-fructose using SMB (Landi and Mantovani, 1975). Illinois Water Treatment Company used an ion exchange resin instead of zeolite.

Many scientists and technologists have studied the ion exclusion process since its inception (Wheaton and Bauman, 1953) about 39 years ago. This process was not used in the sugar industry as it was considered "unrealistic for commercial operation" (Gross, 1971). Problems reported (Schneider and Mikule, 1975) in the literature includes:

1) Highly diluted products results in downstream energy requirement for re-concentration.
2) Jamming and clogging of resin bed by suspended matter.
3) Problems with removal of Ca and Mg from molasses, causing additional waste and costs.
4) Poor resin characteristics, like swelling & shrinking.
5) Difficulties with feeding and removing products.
6) Difficulties in automation of the process.

However, the situation has improved. Progress in Ion exclusion process (Lancrenon and Herve, 1988) is reflected by these developments:

1) Resins with better characteristics.
2) Better ion exchange engineering.
3) Automation resulting in better plant control.
4) Inclusion of waste water treatment (if required).
5) Optimum integration of ion exclusion system in the routine factory or refinery process, if necessary.

2.4.1 Ion Exclusion for Desugarization of Final Molasses.

A simplified explanation of ion exclusion process involved in desugarization is given (Fig. 7). Large size molecules like polysaccharide and coloring compounds are excluded, and removed by the eluent. Ionic substances, such as ash, organic and inorganic acids, and amino acids, are prevented from entering the resin by the Donnan effect and are excluded. Finally, the non-ionized smaller molecules; sucrose, glucose and fructose etc. enter the bead channels. They are physically adsorbed by the effect of van der Waal's forces (Friedrich, 1962). These substances are later desorbed at different times, depending on their affinity for the resin. Normally two products are derived from the ion exclusion process: **Extract**; high in sugars and low in ash, and **Raffinate**; high in ash and low in sugars.

The ion exclusion separation process has proved commercially significant for recovery of sugars from beet

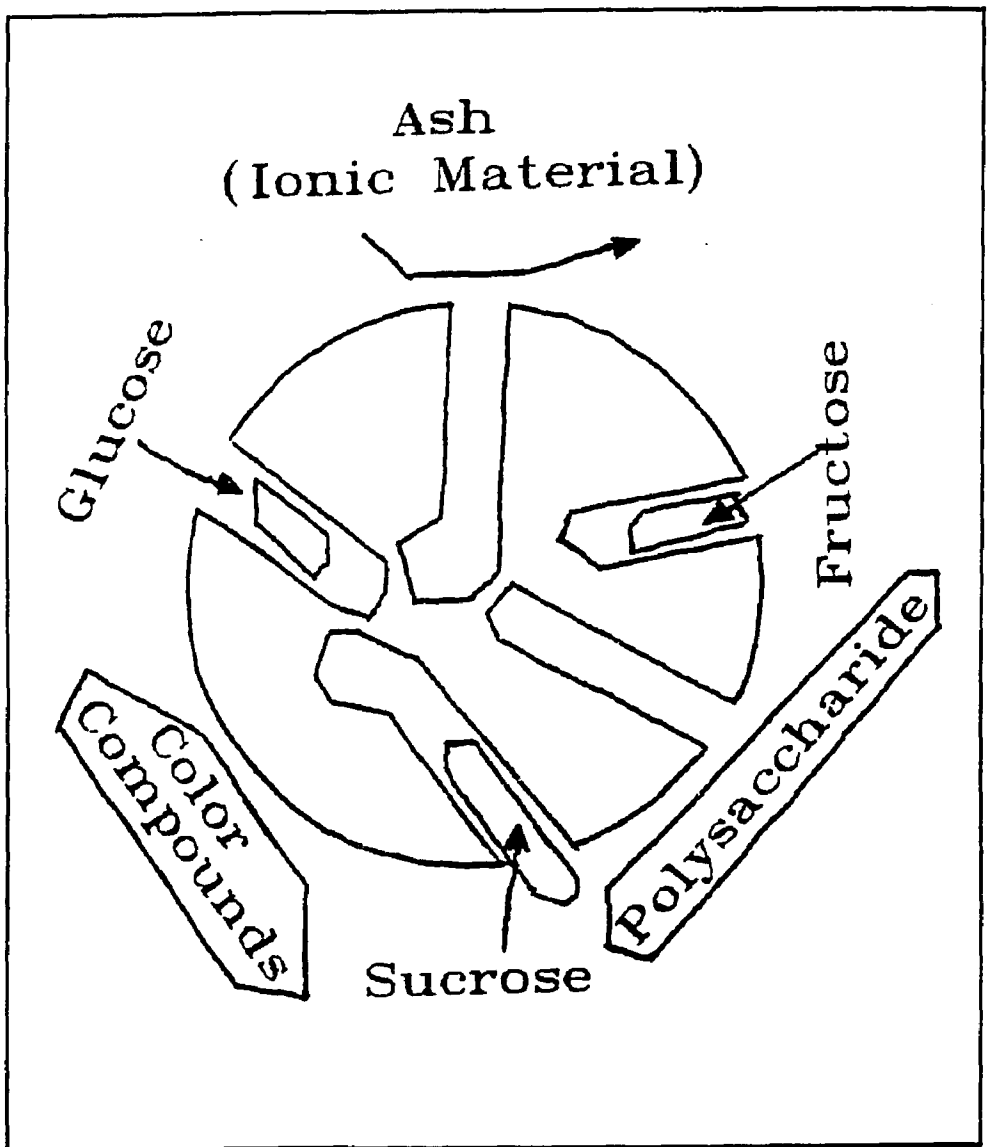

Figure 7: Schematic movement of molasses components around a resin bead. (After Schneider, 1978)

molasses. (Chertudi, 1991; Hongisto, 1979; Herve and Lancrenon, 1989; Gadomski, 1991; Lancrenon and Herve, 1988; Zievers, 1974; Munir, 1976; Schneider and Mikule, 1975). The reasons for its adoption in the beet sugar industry are the greater technical sophistication of that industry and the characteristics of beet molasses. The high level of complex impurities of the cane molasses hinders the successful commercial application of ion exclusion to cane molasses. Comparison of both molasses is given in Table 1. Inorganic constituents of beet and cane molasses are given here for comparison (Table 3). In cane molasses, Ca+Mg is 33.3% of total inorganic constituents whereas, in beet molasses this is only 4.25%.

Table 3:
The inorganic constituents of beet & cane molasses
From Schneider (1978).

On 100 Bx	Beet	Cane
Potassium	3.80	2.7
Sodium	0.70	0.3
Calcium	0.15	1.1
Magnesium	0.05	0.4

There are several industrial units involved in desugarization of beet molasses by ion exclusion in Belgium, France, Germany, and USA (Schoenrock, 1987) but most of them are batch type. Very recently, some plants started working with Simulated Moving Bed technique applying the Ion Exclusion principle (Chertudi, 1991; Gadomski, 1991;

Kakihana, 1989). For cane final molasses, development of the processes on an industrial level, is still under investigation. A comparison of performance of two beet sugar plants, with and without ion exclusion chromatographic system is given in Table 4.

Table 4:
Recovery/loss balance with and without ion Exclusion (I.E.) chromatographic system. (Chertudi, 1991)

a) Twin Falls Factory Data:

	% on beet	% on sugar in beet
Sugar Contents	17.00	100.00
Losses in Molasses	2.33	13.75
Undetermined losses	0.55	3.25
Sugar Recovery	14.12[a]	83.00[a]
I.E.Process Recovery	1.83	10.77
Total Sugar Recovery	15.95[b]	93.77[b]
I.E Molasses Losses	0.50[c]	2.98[c]

b) British Sugar Factory Data:

	% on beet	% on sugar in beet
Sugar Contents	17.11	100.00
Losses in Molasses	1.82	10.64
Undetermined losses	0.69	4.05
Sugar Recovery	14.60[a]	85.31[a]
I.E.Process Recovery	1.43	8.35
Total Sugar Recovery	16.03[b]	93.66[b]
I.E. Molasses Losses	0.39[c]	2.29[c]

a: without Ion Exclusion Chromatographic system.
b: with Ion Exclusion Chromatographic system.
c: loss in Raffinate + loss in crystallization

2.4.2 Resin Characteristics.

The type and quality of resin is of prime importance for successful operation of SMB/Ion exclusion process. Resin quality was one of the causes for early failure of the commercialization of ion exclusion system (Schneider and Mikule, 1975). Resin for exclusion processes should contain ion active groups in a highly ionized form. They should have a relatively open gel structure and be chemically inert. Gel water content, i.e. proportion of water contained in the resin under saturation conditions, is the most important property of the resin. Gel water content of 50-90 % by volume, is considered suitable for use. Capacity of resin to absorb water depends upon Divinyl Benzene contents (DVB). This is termed degree of cross-linkage. The higher the cross-linkage, the less water is absorbed. However, cross-linkage also establishes the physical and chemical properties of the resin. This includes mechanical and thermal stability of the resin. Cross-linkage below 3-4% is considered unstable. Controlling the cross-linkage to the right degree, sugar molecules can enter and leave the resin matrix, but larger molecules, such as color bodies, will be excluded or screened. Ionizable compounds such as sodium and potassium salts, amino acids are excluded at the same time because of the Donnan membrane effect (Norman et al., 1963; Zievers, 1974).

Though a variety of resins are available but only polystyrene resins work well for sugar separation. A cation exchange resin is employed for separation of sugars. The resin has a skeleton of polystyrene. Sulfonic groups are attached chemically to the network of the resin, which has channels of molecular size. Resin beads absorb certain amount of water when immersed in liquid to form a gel-like structure. Diffusion of dissolved substances can take place into and out of the swelled resin.

To avoid ion exchange taking place, potassium, a major cation, present in the molasses should be considered. Ion exchange is detrimental for sugar recovery from molasses as it can supress the Donnan membrane effect resulting more inclusion of salts in high sugar product. Therefore, the resin to be used should be in the potassium form, with a high "diffusion volume", within the resin bead.

A sulphonated polystyrene resin with cross-linkage of 4-8 % and particle size of 50-100 mesh in the monovalent form (Na^+ or K^+) has been used by most workers (Riffer, 1977; Gadomski, 1991; Gross, 1971; Schneider and Mikule, 1975; Maleja et al., 1975; Hongisto, 1977).

2.4.3 Pre-treatment of Molasses.

In order to recover sugars from molasses by ion exclusion (I.E.), suspended and colloidal material, which accounts for 4-6 % (wet volume, % at 50 Bx) of the molasses, (Kakihana, 1989) must be removed. These impurities result

in a gummy and leather-like impermeable layer on the top of the packed bed (Aguirre, 1982). Colloidal particles, on entering the column, will rapidly fill up voids between the resin beads impairing separation efficiency (Hongisto, 1979).

Molasses contains considerable quantities of multivalent ions such as Ca^{++}, Mg^{++}, Fe^{++} (or Fe^{+++}) and Zn^{++} ions etc. and (Table 3). If these are not removed or reduced to reasonable limits they will be exchanged for monovalent ions (sec. 2.2). The effectiveness of resin to achieve the required separation will be reduced. Kakihana (1989) reported that Na+ and K+ form resin can tolerate 500 to 1000 ppm divalent ions. He suggested that diluting molasses to 50 Bx, heating, and then filtering results in a 50% removal of Ca^{++} ions. Weakly acidic cation exchange resin is used to bring down the Ca^{++} ions level to 300 ppm. In beet molasses the Ca-content is about 0.15%, which may not pose any threat, if proper mechanical filtration is carried out. Cane molasses contains a high Ca-content (up to 2.5%), and needs to be reduced to 0.08 - 0.1 % to avoid any ion exchange during ion exclusion process (Hongisto and Heikkila, 1978).

Munir (1976) reported the results of laboratory scale pulse tests on cane molasses. He observed that the ash contents of cane molasses are responsible for the different range of purity (70 - 80) of the extract. It is evident

that purity is about 70 for molasses from Hawaii and S. Africa, while it reached to 77 and 80s for molasses from Brazil and Cuba (Table 5). If divalent ions of the molasses are not reduced to reasonable limits, resin will require frequent regeneration (Riffer, 1977; Zievers, 1974). This becomes essential when it is loaded with Ca^{++} and Mg^{++} to about 15-20 % of its total capacity as shown in Fig. 8. (Schneider, 1978). However there is no mention of purity of the products in the results of these experiments.

Table 5:
Effect of ash contents* on extract purity (Pty).
from Munir (1976).

Cane Molasses	K^+	Na^+	Ca^{++}	Mg^{++}	Pty
Brazil 1972/73	91.1	7.1	24.7	15.5	80
Brazil 1973/74	65.5	2.4	16.3	21.1	82
Hawaii	134.4	10.0	26.6	3.1	70
Cuba	83.7	5.4	27.8	21.7	77
South Africa	111.0	2.8	23.3	30.7	71

* meq/100 g Total Solids.

Regeneration of the resin was required after 25 days of operation in a (beet) molasses separation plant at Mallow, Ireland (Buckley and Norton, 1991). Regeneration itself is a tedious operation. Twelve hours are required for regeneration of the resin bed necessary for percolation of 130 m^3 molasses at 40 °Bx. Backwashing to remove any mud (calcium salts, mainly oxalate) takes another 12 hours, so complete regeneration operation requires 24 hours (Schneider and Mikule, 1975). Other problems associated with

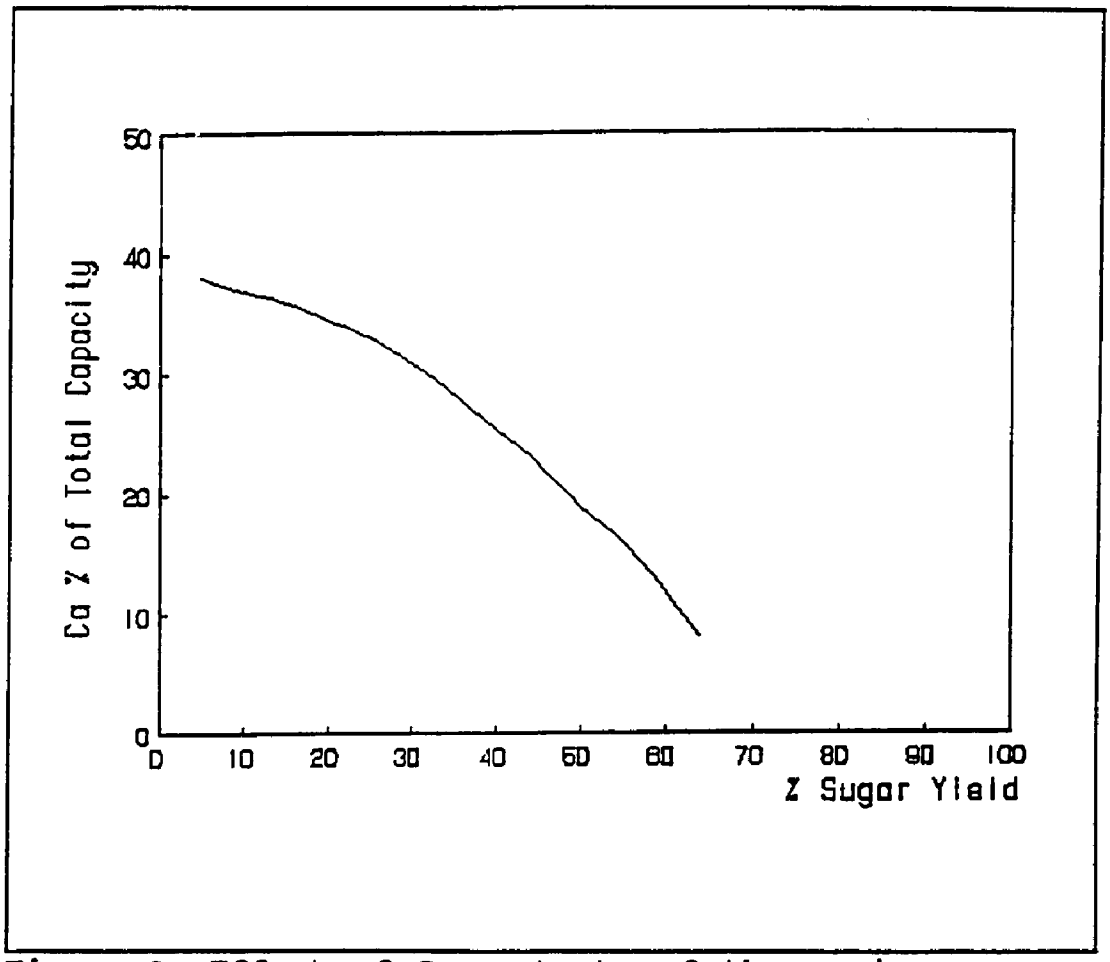

Figure 8: Effect of Ca-contents of the resin on sugar yield. (From Schneider, 1978)

regeneration are economical and environmental. To have a stand-by set of columns involves a lot of capital investment.

Removal of turbidity and other suspended materials to avoid fouling of the column, and filtration of molasses prior to feeding the system has been practiced (Chertudi, 1991; Schneider, 1978; Hongisto, 1979; Hongisto and Heikkila, 1978; Riffer, 1977; Gadomski, 1991; Kakihana, 1989; Schneider and Mikule, 1975; Hongisto, 1977).

Removal of turbidity and calcium from molasses is partially achieved by phosphatation precipitation of molasses. By this treatment, other impurities are also adsorbed on the developing phosphate precipitates. It has been observed that by combining dilution and filtration, phosphatation removes 80-90 % hardness from molasses (Schneider, 1978; Hongisto, 1979; Hongisto and Heikkila, 1978; Hongisto, 1977; Aguirre, 1982). To remove the remaining hardness, phosphatation is followed by ion exchange or deliming. Phosphatation, when followed by ion exchange, results in 8-10 fold ICUMSA reduction in color (based on molasses color) of the treated molasses.

Formation of calcium oxalate along with other calcium salts on ion exchange resin in columns has been reported when phosphatation clarification method is applied to molasses. Backwashing (Schneider and Mikule, 1975) and pH adjustment in the range of 5.2 to 5.5 (Schneider, 1978) have

been recommended to overcome this problem. Phosphoric acid must be used in precise amount (11 to 12 g/l of 45 brix molasses) determined for each batch of molasses. Additional phosphoric acid only increases the cost of treatment and volume of the precipitate (Table 4). The cost of phosphoric acid is a major expense of the ion exclusion process. As the precipitates formed are too small to filter easily, addition of polyelectrolyte flocculent has been suggested (Aguirre, 1982).

Table 6:
Effect of % H_3PO_4 on mud volume (cane molasses).
(Schneider, 1978)

% H_3PO_4	Mud % on dry substances
0.25	8 - 12
0.50	15 - 20
1.00	25 - 30
1.50	30 - 40

Gadomski (1991) proposed a multistage pH controlled chemical precipitation to reduce the hardness to less than 750 ppm. It is a treatment of beet molasses with soda ash and sodium hydroxide to precipitate calcium as carbonate and magnesium as hydroxide.

Chertudi (1991) suggested two alternatives for the reduction of hardness in feed for exclusion system. First is the softening of molasses with weak cation exchange resin. The other is to treat thin juice with a weak cation

exchange system. This will result in a molasses with acceptable ash contents for separation purpose.

2.4.4 Quality and Post-Treatment of SMB/I.E. Products.

Riffer (1977) took the advantage of solubility difference between sugars and colorant molecules when the pH of the cane molasses is reduced to 4. The secondary effect of this is salting out effect due to hydration of added acids. By this technique a liquid syrup, with 10% color and 50% ash of the original molasses, was produced.

Some of the workers suggested that to recover total sugars, opposed to sucrose only, in the molasses is more beneficial and it is better utilization of the system. It has been observed that when crystal sugar is desired as the end product, recovery of sucrose is in the range of 60-90 % (Hongisto and Heikkila, 1978; Zievers, 1974; Munir, 1976). But with the same system, the recovery of sugars (total) is in the range of 85 to 95 % (Chertudi, 1991; Hongisto, 1979; Hongisto and Heikkila, 1978; Gadomski, 1991; Munir, 1976; Hongisto, 1977). Different alternatives have been suggested to maximize recovery of sugars from molasses. Riffer(1977) suggested as that sucrose, glucose, & fructose strongly inhibit crystallization of each other, it is better to recover the sugars of molasses in liquid form.

Hongisto and Heikkila (1978) suggested three alternatives for desugarization of cane molasses. First alternative is the separation of molasses into two products,

i.e sucrose and secondary molasses which contains invert and non-sugars. In the second alternative sucrose can be recovered in crystallized form and invert as liquid. This yields 92 % recovery of sugars. Another alternative is that molasses is inverted prior to feeding the system. This can be explained that nonsugars, sucrose, glucose and fructose, all emerge out of system, at different timings because of difference in their respective distribution coefficients, which is greatest for nonsugars and fructose. Because of a clear separation of nonsugars and monosaccharides, molasses inverted before feeding yields in an increases capacity of the system. This has been reported that with this arrangement 18 tons (dry solids) molasses can be treated on the same column which has a capacity of 8-10 tons (dry solids) of noninverted molasses. This will raise the capacity of the system by 2.25 times (Hongisto, 1979). Hongisto and Heikkila (1978), suggested treating the extract to convert to liquid sugar after proper demineralization & decolorization.

Extract purities reported are in the range from 87-94 and 79-94, for beet and cane molasses respectively. The amount of eluent (water) dominates the performance of SMB separation process. By changing the water/feed molasses ratio, extract purity and recovery can be adjusted. SMB process can be operated for high purities when cane juice purities are low (in the beginning and at closure of

campaign). Similarly, it can be operated for high recoveries when cane juice purities are high (Kakihana, 1989). This is to maintain the purities of the syrup high enough to follow appropriate boiling schemes on pan floor. Extremely low purity of the extract should be avoided as recycled nonsugars accumulated in the process will have negative effect on sugar boiling. Extract from SMB process can either be mixed with thin juice stream (Kakihana, 1989; Schneider and Mikule, 1975), or sent directly for crystallization (Chertudi, 1991). SMB extract has 50 % betaine recycled, compared to Steffen process. In case of liquid sugar as final product, extract is demineralized and decolorized by conventional ion exchange systems. Thus a product of 50-200 ICUMSA units and 0.03-0.05 % ash contents is possible (Hongisto, 1977). Hongisto (1979) suggested production of household syrup with high color (1000 ICUMSA units) will reduce operational costs.

Purity of raffinate (low sugar fraction of SMB/Ion Exclusion process) ranges from 5-30, and 10-39 for beet and cane molasses, respectively, (Chertudi, 1991; Schneider, 1978; Hongisto and Heikkila, 1978; Kakihana, 1989; Schneider and Mikule, 1975). For beet molasses, it is evaporated to 50-70 Bx and mixed with beet pulp, or sold as fodder molasses (Chertudi, 1991; Gadomski, 1991).

2.4.5 Other Parameters of Importance.

Other parameters of importance are concentration of feed, temperature, pH, and flow rates.

The internal pore space available to accommodate a certain volume of feed is fixed. So maximum volume of feed is determined by volume of resin. Munir (1976) working with beet molasses recommended feed purity around 59-61 to avoid any overloading with sugars or nonsugars. There is another basis to assess the feed volume and that is "load on column". It is the amount of nonsugars for a particular volume of resin in particular time. Kearney (1990) has suggested a load in the range of 160-250 kg nonsugars/m^3/day. According to this recommendation, for desugarization of 100 tons of a typical beet molasses as feed (65% sugars and 60 Brix), about 37 m^3 resin will be required at rate of 200 kg nonsugars/m^3/day.

A proper range of temperature is necessary for best results. At a high temperature, separation is enhanced because of lower viscosity and faster diffusion rates. Temperatures above 70 °C help to suppress microbial growth in the system. On the other hand temperatures above 90 °C adversely affect the cross-linkage of the resin. It causes deterioration of sugar, Maillard reaction and caramelization. Most workers have selected temperature of 80 - 90 °C (Riffer, 1977; Gadomski, 1991; Zievers, 1974; Munir, 1976; Gross, 1971; Schneider and Mikule, 1975;

Hongisto, 1977; Gross, 1971; Hartmann, 1982; Kearney, 1990).

pH has its own role in the separation process. A certain limit of pH is maintained to avoid inversion of sugars at low pH. After-precipitation of salts in molasses feed will take place, if pH is on alkaline side. Working range of pH is from 6.5 - 7.5 (Schneider, 1978; Gadomski, 1991; Schneider and Mikule, 1975)

Flow rates effect the separation process. Flow rate can be varied within a certain range to suit the separation conditions. Though lower flow rates favor equilibrium conditions but these should be fast enough to push the sugars and nonsugars to the appropriate exit port in the desired time to have an optimum separation (sec. 2.3.3). Too fast flow rates will not permit the solutes to diffuse into the resin and then be eluted at different timings, thus separation will be effected.

Work done by various researchers on desugarization of molasses (beet and cane) has been summarized in Table 7.

Table 7:
Summary of Desugarization of beet/cane molasses by various investigators.

Worker	Process	Feed Mol.	Feed Brix	Feed Pty	Temp °C	Pre-Treatment	Prod Brix	Prod Pty	Rej. Brix	Rej. Pty	Recovery %
Steffen Process (1883)	Lime-Suc. pptn.	Beet	5-12% Sucr.	X	<18 & 90	No tmnt.	X	90-95	X	60	60-82
Stark (1967)	I.E./ Batch	Beet Cane	50 50	65 40	25 & 90	X	X	>80 >68s	X	12-34	50 65
Gross (1971)	I.E./ Batch	Beet Cane	50 50	X X	80 80	Demineral. No tmnt.	15 15	96 93	X X	X X	50
Zeivers (1974)	I.E./ Batch	Beet	60	63	80	Filtration	15	89	X	X	75 sg.
Schneider (1975)	I.E./ Batch	Beet	40-60	63	80-85	Mechanical Filtration	15	87	5	32	74
Munir (1976)	I.E./ Batch	Beet Cane	70	60	90	Demineral.	10-11	90 80-85	X	X	95 sg. 85 cryst
Hongisto (1976)	I.E./ Batch	Beet Cane	30-40	X X	65-90	Mechanical Filtration	17	87-94	5	5-25 on DS	87 sg.
Riffer (1977)	I.E./ Batch	Cane	50	X	80	pH adjust-ment to 4	21-23	X	X	X	X

...contd Table 7:

Worker	Process	Feed Mol.	Feed Brix	Feed Pty	Temp °C	Pre-Treatment	Prod Brix	Prod Pty	Rej. Brix	Rej Pty	Recovery %
Schneider (1978)	I.E./ Batch	Cane	X	X	X	Phosphatn, Ion Exchange	X	91	X	39	70 sg.
Hongisto Heikkila (1978)	I.E./ Batch	Beet Cane	40	X	X	Phosphatn centrifuge Separation	5 S 8 I	79 7.5	6	10	92 sg. 75 > 88 cryst.
Hongisto (1979)	I.E/Batch Liq. Sugar	Beet Cane	X	X	X	Phosphatn. Filtn.Deliming	15 11	95 93	6 5	21 20	85 90
Aguirre (1982)	I.E./ Batch	Cane	39	55	80	Acid Inversion	13	96 88	8-10	8-39	49 92
Kakihana (1989)	I.E./SMB	Cane/ B.Mol	50	X	75	Dilution/ Decan Ion-Exch.	30-35	80-85	8-10	15-18	76-91
Kearney (1990)	I.E./SMB	Beet	X	60	80	Dilution, Softening	X	93	X	X	> 90
Gadomski (1991)	I.E./SMB	Beet	X	75	65-75	Dilution Softening	30	90	4-8	X	90
Chertudi (1991)	I.E./SMB	Beet	50-70	50-70	X	Dilution, Ion-Exch.	35	92	5	7	87-90

X = no information available;I.E.=Ion Exclusion;SMB=Simulated Moving Bed; Prod=Product; Rej=Reject;Suc/S=Sucrose;I=Invert;sg=Sugars; Cryst=Crystals; Demineral=Demineralization;Mol=Molasses;Mech.Filtn=Mechanical Filtration; pptn=Precipitation;DS=Dry Solids;Pty=Purity;Decan=Decantation.

Chapter 3

OBJECTIVES

It was the primary objective of this study to investigate the possibilities of application of SMB ion exclusion chromatography for recovery of sugars from cane molasses by using a new generation of resins with better characteristics in a pilot plant. (sec. 2.4.) Like for any other chromatographic process an experimental study of the equilibria in the system involved is imperative for the modeling and design of SMB Ion Exclusion operation. It is crucial to study the properties of the adsorbent which then leads to the selection of most appropriate parameters for the continuous operation.

In this regard the secondary objective of this study is a) to provide a quantitative description of the equilibria of the system through equilibrium isotherms, and b) to study the kinetics of the system.

The following scheme was followed to achieve the objectives of this study.

Phase I. Equilibria study:

- Pulse testing experiments with single/binary/multi components mixture such as glucose, fructose, sucrose, potassium chloride, High Fructose Corn Syrup (HFCS) and (pre-treated) final molasses.

- Matching the experimental profiles with those calculated from a local equilibrium model.
- Establishing the value of K, isotherms for different components of molasses such as sucrose, glucose, fructose, and salts.

Phase II. Kinetics Study:

- Determining the rate of mass transfer and Height Equivalent to Theoretical Plate (HETP).

Phase III. Establishment of parameters for continuous operation.

- Establishing the parameters for continuous experiments by running a simulation program of the SMB process based on information from pulse testing.
- Selecting the most appropriate parameters from simulated data for continuous experiments on molasses as feed.

Phase IV. Separation on SMB Pilot Plant.

- To run continuous experiments with molasses (pre-treated with a standard phosphatation method with modification of Vortex Flow Filtration treatment) as feed with parameters selected in Phase III.
- To optimize the parameters.

Phase V. Post treatment of products.

- Post treatment of products obtained from SMB experiments, including concentration, decolorization and crystallization.

Chapter 4

MATERIALS AND METHODS

4.1 Materials.

4.1.1 Chemicals.

Various standard compounds used for this study were: Glucose, Fructose, Potassium Chloride, Calcium Chloride, and Dextran. (Sigma Co.) Sucrose; Commercial grade. High Fructose Corn Syrup. Commercial grade. (Composition of HFCS as analyzed in our laboratory by HPLC was as: Glucose 48.72%; Fructose 38.15%; disaccharides 3.39%; and Others 9.74%).

Cane Final molasses, from Louisiana sugar mills. Composition of the molasses used in this study is given in Table 17.

Resin DOWEX monosphere 99 CA, a polystyrene divinylbenzene based resin (particle size 0.32 mm, 6% Cross-link) in Ca^{++} form was used for pulse testing only. It has an ion exchange capacity of about 2.5 meq SO_3- group per liter wet resin.

Resin XUS-40166.00, a cation exchanger in K^+ form was used for pulse testing and continuous experiments. It is a polystyrene-divinylbenzene based resin with an approximate degree of crosslinkage of 6% and a volume based median pore size of around 10 Å. It has an ion exchange capacity of about 3.2 meq SO_3- groups per liter wet resin and a volume

based median particle diameter d_p of 390 mm. (Dow Chemical Co.)

A combination of resins provided by Applexion, Harvey, IL, was used for decolorization and deionization of extract from SMB system. It include the following types: a polystyrene resin with Ketone group, ADS 1/1; a cation exchange resin, XA 100/1; an anion exchange resin, XA 47/1.

ADS 1/1 acts as adsorbent. Low molecular weight (up to 400 m.w.) colorants will be adsorbed by this resin. No ion exchange will take place. XA 100/1 resin in H^+ form, will retain a part of malenoidines, a major form of coloring matter which acts as basic nonsugar. Also a part of caramels, another form of colorants present in molasses, will be retained by this resin. XA 47/1 resin in OH^- form, will retain third form of coloring matter, products of alkaline dehydration of hexose (PADH) which are mostly acidic coloring matter. A part of caramels will also be retained by this resin.

Chemicals used for pre-treatment were:

Phosphoric acid and Sodium Hydroxide of analytical grade. Talosep, a commercial polyelectrolyte by Tate & Lyle. This is a high molecular weight (MW > 10^7) polyacrylamide polymer. Deionized water was used for all experimental work.

4.1.2 Experimental Equipment.

4.1.2.1 Pre-treatment Equipment.

EDTA Titration Equipment.

A titration equipment (by Radiometer, Copenhagen) was used to analyze the hardness of molasses. It consists of the following units: i) Autoburette ABU 12, ii) Titration Assembly.

Standard method of EDTA was used for determining hardness of molasses samples.

Heating, Evaporation.

These operations were performed by using facilities of LSU Audubon Sugar Mill.

Membrane Filtration Unit.

Benchmark GX is a vortex flow filtration system made by Membrex, Inc. Fairfield, NJ. It consists of an electronic control unit which houses the motor, displays and microprocessor and a rotary separation unit which holds the membrane cartridge. This unit was used to filter molasses after chemical treatment with a stainless steel filter of 0.1 μ size. Area of cartridge was 200 cm^2. The capacity of this unit is 50 l/m^2/hour at nominal conditions.

4.1.2.2 SMB Pilot Plant.

Pilot plant at Audubon Sugar Institute was provided by Applexion, Harvey, IL. It consists of eight identical glass columns (210 L x 6 ID, volume 5.94 l). (Fig. 9). Each column is provided with a jacket for temperature control by

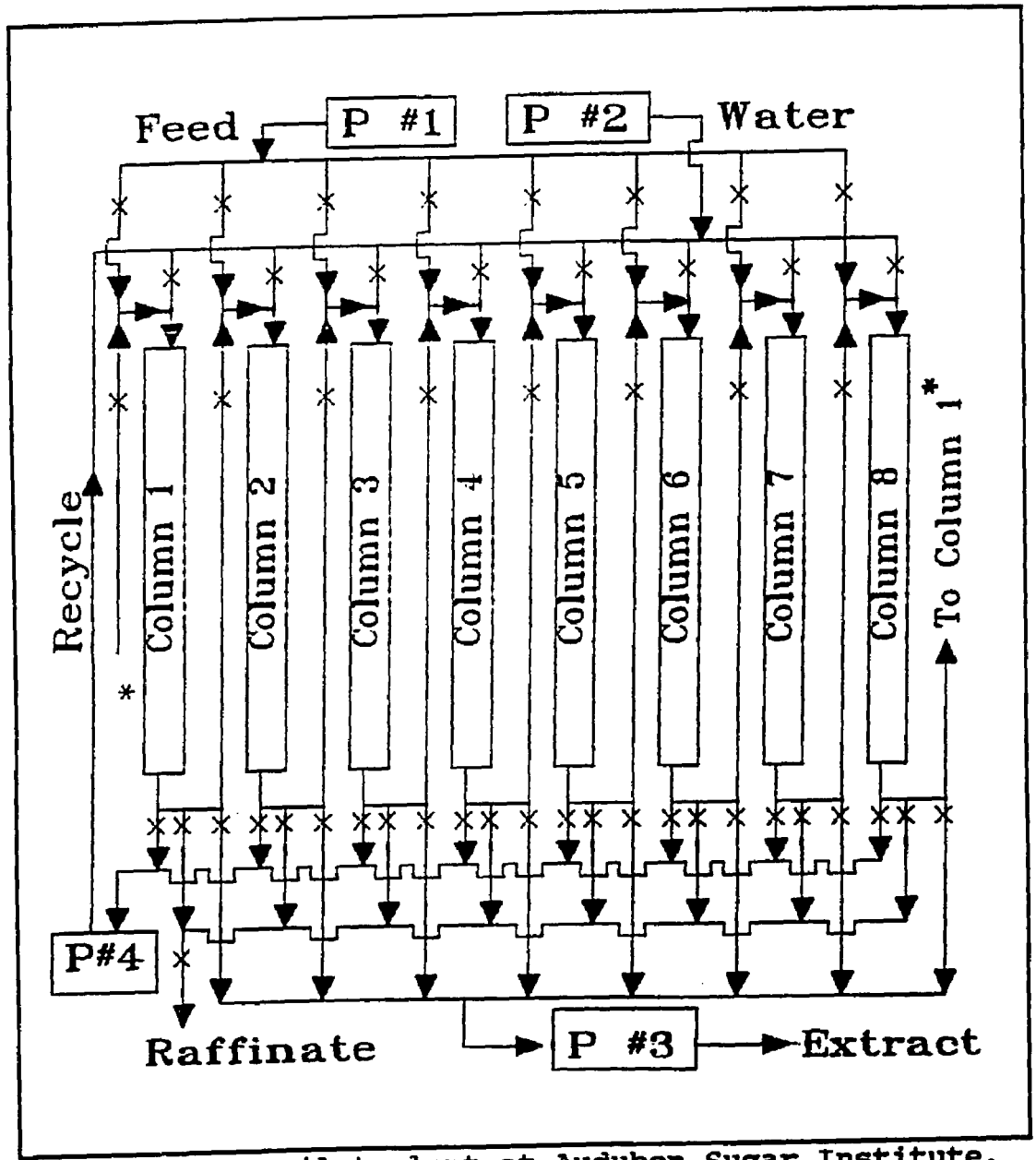

Figure 9: SMB pilot plant at Audubon Sugar Institute. P is pump, x is valve in the line and arrow show the direction of flow of fluid.

flow of hot water through it. Columns are connected in series by solenoid valves. These valves can be operated manually for pulse testing, otherwise operated by a computer program. Eccentric screw type pumps, a part of the system are designed to deliver a constant flow rate of feed (molasses), eluent (water), recycle (dilute fraction of sugars + salts), and extract (high sugars product of system) independent of back pressure. Raffinate (High salts product) flow rate is by the difference of flow rates of input and output.

Feed and eluent water are introduced at the top of columns to flow downward in order to avoid fluidizing the resin which might cause attrition of the resin (McCabe & Smith 1967), also it can cause extra band broadening and worsen separation. Products and recycle emerge from the bottom of the column and extracted continuously through the loops provided for the purpose. In a SMB operation, sequencing of feeding and extraction ports, to next column is controlled by computer program (sec. 4.2.4)

4.1.2.3 Post-treatment Equipments.

Decolorization of extract:

5.0 cm I.D X 60 cm L glass columns, packed with appropriate resins (sec. 4.1.1) were used as shown in Fig. 10.

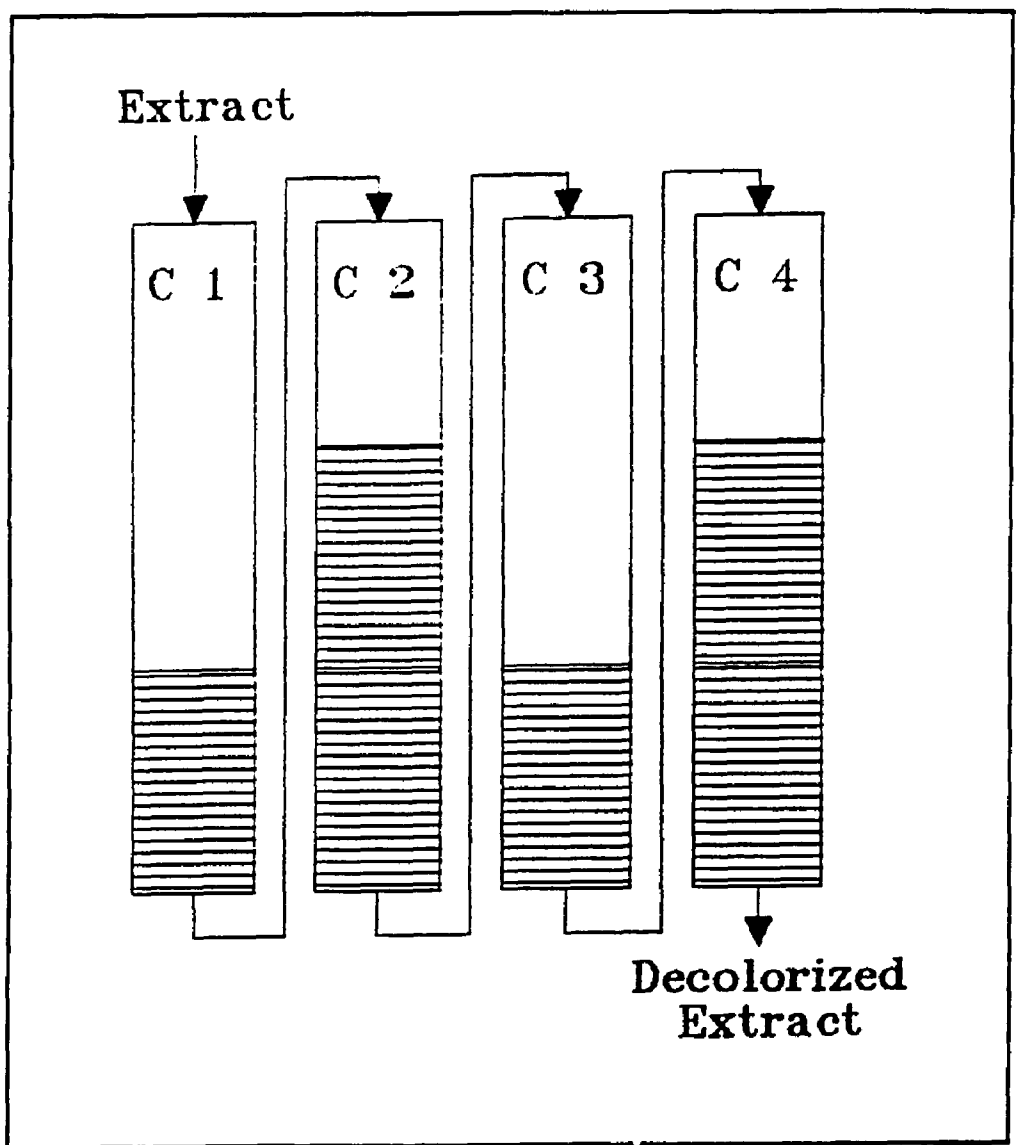

Figure 10: Decolorization arrangement of the extract. Columns C1 and C3, adsorbent resin ADS1/1 (bed volume, .5 l); column C2, cation exchange resin XA100/1 (bed volume, 1 l); column C4, anion exchange resin XA47/1 (bed volume, 1 l).

4.1.3 Analytical Equipments/Methods.

High performance liquid chromatography (HPLC) equipment.

HPLC is the preferred method and is currently under considereation for approval by International Commission of Uniform Methods of Sugar Analysis (ICUMSA) as standard method for determination of sucrose, glucose, fructose and other sugars in a sugar solution. This method also provides semi-quantitative information on the salt and organic acids components sugar solutions (Pynnonen, 1991). The experimental arrangement included the following:

A solvent delivery system (Water 6000, flow rate 0.5-0.9 ml/min), an injector (Water 712, 20 µl volume), an analytical column (Bio-rad, Model HPX-87N. 300 x 7.8 mm packed with sodium form sulfonated divinyl benzene-styrene copolymer, particle size 9 µm, and Model HPX-87K, 300 x 7.8 mm packed with potassium form of same resin), a detector (a differential refractometer, Waters model 410), and an integrator/recorder (Spectra-Physics model SP 4270).

Sample preparation: Samples were diluted to 0.1-0.2 % by dissolving in 0.1 M K_2SO_4 solution. K_2SO_4 was used to avoid overlap of water and salts peaks, which appears almost at the same time. The samples was filtered through 0.45 micron millipore filter before injection to the system.

In this study, the column used in HPLC analysis was packed with resin in Na^+ form for Runs #1 to #4 (later it was replaced with potsassium form) so there are chances of ion

exchange to take place, which may cause an error for the detector and then later in the chromatogram. Another possible error is that the response factor (RF) was not calculated to measure the concentration of the components from the peak area percentage, rather peak area percent was assumed as percent concentration of the component.

Refractometer

i) ABBE Model of American Optical Corporation was used for higher brix solution of concentration >0.1.

ii) Differential refractometer Model DD-5, by ATAGO Co. was used lower brix solutions of concentration <0.1.

Basic principle of this equipment is that the index of refraction of a solution depends on its concentration and temperature. Refractive Index (RI) of the solution is converted by the instrument to percentage of solids. Total solids are calculated as equivalent sucrose leading to increased error with decreased purity.

There is a possible source of error while measuring brix with this refractometer. This equipment is calibrated for pure sucrose solution to give the total dissolved solute components (Wt %). For impure solutions, the refractive index should be converted to concentration (Wt %) using functions relating the refractive index and concentration (Tables sec. 4.1.4).

Polarimeter

Automatic Saccharimeter Model Autopol II S, by Rudolph Research was used to read pol of sugar solutions. It supplies information of the approximate concentration of sucrose in the solution.

pH Meter

Digital Ionalyzer Model 601/A by Orion Research was used for pH reading of different sugar solutions.

Spectrophotometer

Spectronic 20 (Bausch & Lomb) wavelength at 420 nm, was used to measure the color of the sugar solutions as specified by ICUMSA.

Conductivity Meter

Model 1710, BIO-RAD. This unit was used to read conductivity of different solutions, specifically after decolorization of extract.

Flame Photometer

Model JENWAY PFP7 by BUCK Scientific, Inc. A potassium (K) filter was used for the analysis of the resin.

4.1.4 Tables.

The following tables were used to get density of KCl, sucrose, glucose, and fructose solutions used in this study.

1) CONCENTRATIVE PROPERTIES OF AQUEOUS SOLUTIONS: CONVERSION TABLES by A.V. Wolf, Morden G. Brown and Phoebe G. Prentiss in Handbook of Chemistry and Physics, 53rd Ed., 1972-1973, CRC Press, Cleveland, Ohio.

2) TABLE 16 in Cane Sugar handbook by Meade and Chen 1977, 10th Ed. John Wiley & Sons, New York.

4.2 Methods/Procedures.

4.2.1 Characterization of Resin: Theoretical Consideration.

To evaluate a continuous chromatographic system, on bench or pilot scale, is expensive and time consuming. A simple and reliable method is needed to predict performance of a system in a continuous operation. Pulse testing on a fixed bed system helps to understand the properties of an adsorbent i.e. mass transfer rates and adsorption equilibrium. (de Rosset et al. 1976). It has been recommended that pulse testing be done on a continuous system or a scalable pilot to evaluate the properties of the adsorbent. This then helps to understand the effects of band broadening from column connections and column packing characteristics (Saska et al. 1991).

For large scale liquid chromatography, pulse test procedures are analogous to conventional analytical procedures. Pulse testing uses adsorbent of commercial size. This results in a small pressure drop, allows relatively larger "sample injection" and on-line analysis of effluent emerging from the column. Distribution co-efficients can be obtained by matching the experimental profiles with those calculated from a theoretical model.

Pulse Testing on Ca^{++} & K^{+} Resin:

For an optimum design of SMB operation for desugarizing molasses, it is crucial to understand the separation characteristics of the resin (e.g. equilibria) for the different components of molasses. The main components include **sucrose, glucose, fructose, salts, colorants, polysaccharides etc.** Unfortunately no work has been reported in literature about the performance of the new generation of strong cation exchange resins in K^{+} form, in spite of the fact that these resins have been in commercial use in the USA for last three years.

To validate our pulse testing of the K^{+} resin we considered it necessary to test the procedure on a resin for which information is available in the literature. A detailed work has been reported on strong cation exchange resins in Ca^{++} form used for commercial separation of glucose and fructose. Therefore the Ca^{++} form of the resin was selected to verify the pulse testing procedure on the pilot plant to be employed for desugarizing of the cane molasses.

4.2.1.1 Pulse Testing on Resins.

Pulse testing was done on 6 or 7 columns (L=210 cm, ID=6 cm and 5.940 L volume each) that form a part of the SMB pilot plant. The solenoids valves (Fig. 9) were mannualy configured such as to connect the columns used in pulse testing in series. The system was packed with DOWEX99 CA, a strong cation exchange resin in Ca^{++} form. The system was

heated and kept at 70 ^{0}C by circulating hot water through the columns jackets. About 300 (±1) grams of fructose/glucose solution, of various concentrations, (Table 11) was introduced at the top of first column by the feed pump. Then the components were eluted by hot deionized water (flow rate 120-160 ±3 ml/min). Elution time was measured from the moment the water pump was turned on. Samples were taken periodically in small quantities (compared with the total volume in the system) so as not to effect the flow rate through the system. These samples were drawn after two, four, and six or seven columns, respectively. This was to determine the values of Height Equivalent to Theoretical Plate (HETP) by difference from the response signals from the experiment to avoid introducing the assumption of a perfect pulse injection. These samples were analyzed for concentration off-line. HPLC analyses were done in the case of binary and multicomponent feed.

When resin was tested at high loads, column number one (runs 5 and 11) and one and two (runs 6 and 12) were fed until the outlet reached the inlet concentration and then these columns were connected to the rest of the columns and elution was started as before. Thus these columns served as "feed reservoirs."

Height Equivalent to a Theoretical Plate:

Height equivalent to a theoretical plate (HETP) is an empirical quantity, which is of much practical value to

calculate the effects of the length of column and the feeding techniques on the separation obtained. Thus it is helpful to consider the chromatographic column as equivalent to a number of discrete equilibrium stages or plates for the analysis and design of continuous counter current adsorption process.

HETP is estimated from chromatographic measurements for similar hydrodynamic conditions in a fixed adsorbent bed (deRosset et al.,1978).

HETP values depend on the nature of the substances to be treated and the flow rates (Wankat, P.C. 1986). These values can be changed either by changing the particle size or by viscosity of the solvent. Minimum value of the HETP is preferable as it will result less zone spreading allowing use of large feed pulses and reduce the time between the feed pulses. However, there is a limit of reduction of inefficient regions even with infinite number of theoretical plates (N). The ultimate objective is to have minimum inefficient region and maximum capacity of the system (Wankat, 1986)

The means (t′) and variances (σ^2) of elution peaks were calculated from the following expressions to evaluate the effective HETP:

$$t' = \int ctdt \,/\, \int cdt \qquad (4.1)$$

$$\sigma^2 = \int c(t-t')^2\, dt \,/\, \int cdt \qquad (4.2)$$

$$HETP = L_E\, (\sigma/t')^2 \qquad (4.3)$$

To take into account the effective length of column L_E, the total column length L, was corrected for the length of the feed "plug" L_F by the following expression:

$$L_E = L_T - \tfrac{1}{2} L_F$$

$$L_F = m_F / (\rho \epsilon A)$$

$$L_E = L_T - \tfrac{1}{2} m_F / (\rho \epsilon A) \qquad (4.4)$$

m_F, mass of feed; ρ,density of feed; ϵ, void volume of the system; A, cross-sectional area of the column.

Contrary to some previous reports, it was observed that at industrial concentrations (>40-50 %), the isotherms were non-linear and coupled, so the distribution coefficients that describe the relationship between the concentration of the component in the resin and in the solution at equilibrium were assumed of the form:

$$K_i \equiv q_i/c_i = K_{i0} + A_i c_i + B_i c_j \qquad (4.5)$$

$$K_j \equiv q_j/c_j = K_{j0} + A_j c_i + B_j cj \qquad (4.6)$$

where K_{i0}, K_{j0}, A_i, and B_j are the coefficients applicable for single component feed. A_j and B_i are the coefficients for binary feeds. c, liquid concentration g/100 ml; q, concentration in resin g/100 ml resin; i for component 1 and j for component 2.

The coefficients for glucose and fructose were obtained by matching the experimental profiles with those calculated from a local equilibrium model:

$$\delta c/\delta t + ((1 - \epsilon)/\epsilon)\, \delta q/\delta t + v(\delta c/\delta z) = 0 \qquad (4.7)$$

Equations were solved using the method of finite differences. The time t (0.8 min) and spatial interval z (10 cm) were selected to closely correlate the low concentration pulse responses. By choosing these experimental conditions the effects of kinetics of the adsorption process such as mass transfer and other dispersive effects were taken into account.

The infinite dilution distribution coefficients for glucose and fructose (K_{G0} and K_{F0}, respectively) were determined by matching the low concentration (<1%) single component feed profiles with those calculated, while the concentration dependent terms A_G, A_F, B_G and B_F were considered to be equal to zero.

A_i and B_j were obtained from single component runs of higher concentrations (15-60 w%) with $A_j = B_i = 0$. Cross coefficient A_j and B_i were obtained from High Fructose Corn Syrup (HFCS) runs of concentration 10-60 w%.

ϵ, the void volume for the system (which includes the column connections valves etc.), and for the individual columns was determined by pulse tests with a high molecular weight dextran solution at the same temperature as for other runs, i.e. 70 ^{0}C. The ϵ was calculated as:

$$\epsilon = \frac{Q \times t'}{B.V.}$$

where Q = Flow rate of eluent, ml/min
t' = Retention Time, min and
B.V. = Total Bed Volume, ml

Pulse testing on K^+ resin:

The same procedure as for Ca^{++} form of resin was adopted for pulse testing on the K^+ form resin to determine the distribution coefficients of glucose, fructose, sucrose, and potassium chloride (for non-sugars of molasses). In some experiments molasses were used as feed for pulse testing.

For single component feed, pulse testing was done on two-in-series columns. For binary component-feed and molasses, four columns were used for pulse testing. In addition to off-line sampling as in case of Ca^{++}, effluent was monitored on-line by preparative Refractive Index (RI) detector. This was done only for low concentration runs because of its limited range.

The cross co-efficient was determined only for 1:3 potassium chloride/sucrose binary feeds.

Various temperature (30, 50, and 70^{0}C) and flow rates (50 to 350 ml/min) were tested to study their effect on the different characteristics of the resin.

4.2.2 Establishment of Parameters for Continuous Experiment: Theoretical Considerations.

As discussed before (sec. 2.3.3) 8 columns of the SMB pilot plant were divided into four zones based on the position of the process streams described as below:

Zone I 1 Column.

Zone II 3 Columns.

Zone III 2 Columns.

Zone IV 2 Columns.

The difference in flow in each of these zones is associated with the process stream flow rates, entering and exiting the system. Flow rate in each of the zones is as:

Zone I = $Q_{Zone\ II} - Q_B$

Zone II = $Q_{Feed} + Q_{Zone\ III}$

Zone III = $Q_{Zone\ IV} - Q_A$

Zone IV = $Q_{Eluent} + Q_{Recycle}$

The separation profile for desired purity and recovery can be modified to suit the demandss of the separation. This can be achieved by varying the process parameters and/or the number of sections per zone.

The average values of K, the distribution coefficient, derived from the pulse testing of different components on XUS-40166.00 in K^+ form were used to run a simulation program[1] for continuous experiment. Other parameters were kept the same as in the experiment (switch time, 8.6 min; Q_{Feed} = 20 ml/min; Q_{Water} = 120 ml/min; $Q_{Recycle}$ = 250 ml/min; $Q_{Extract}$ = 30 ml/min; $Q_{Raffinate}$ = 110 ml/min). Based on the output of simulation data, concentration profiles (Fig. 11-14) of the system were drawn. From these, most appropriate parameters including the flow rates of feed, eluent, extract and raffinate, (and flow rates in different zones of the system) switch time, were selected. Later on these parameters were

[1] Computer modeling and simulation part of this study is by the courtesy of Dr. Saska. (Publication in press)

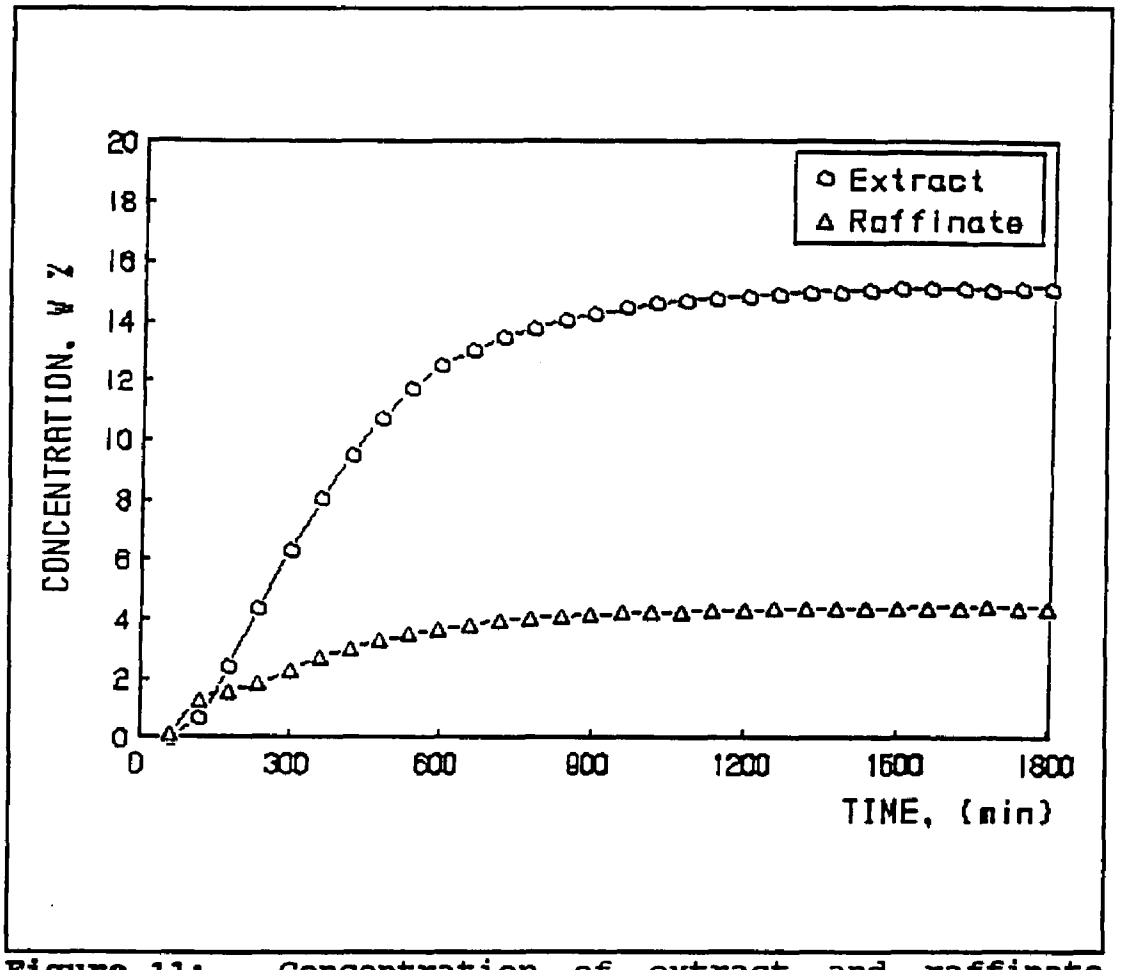

Figure 11: Concentration of extract and raffinate (simulated data, with starting conditions as of Run #4)

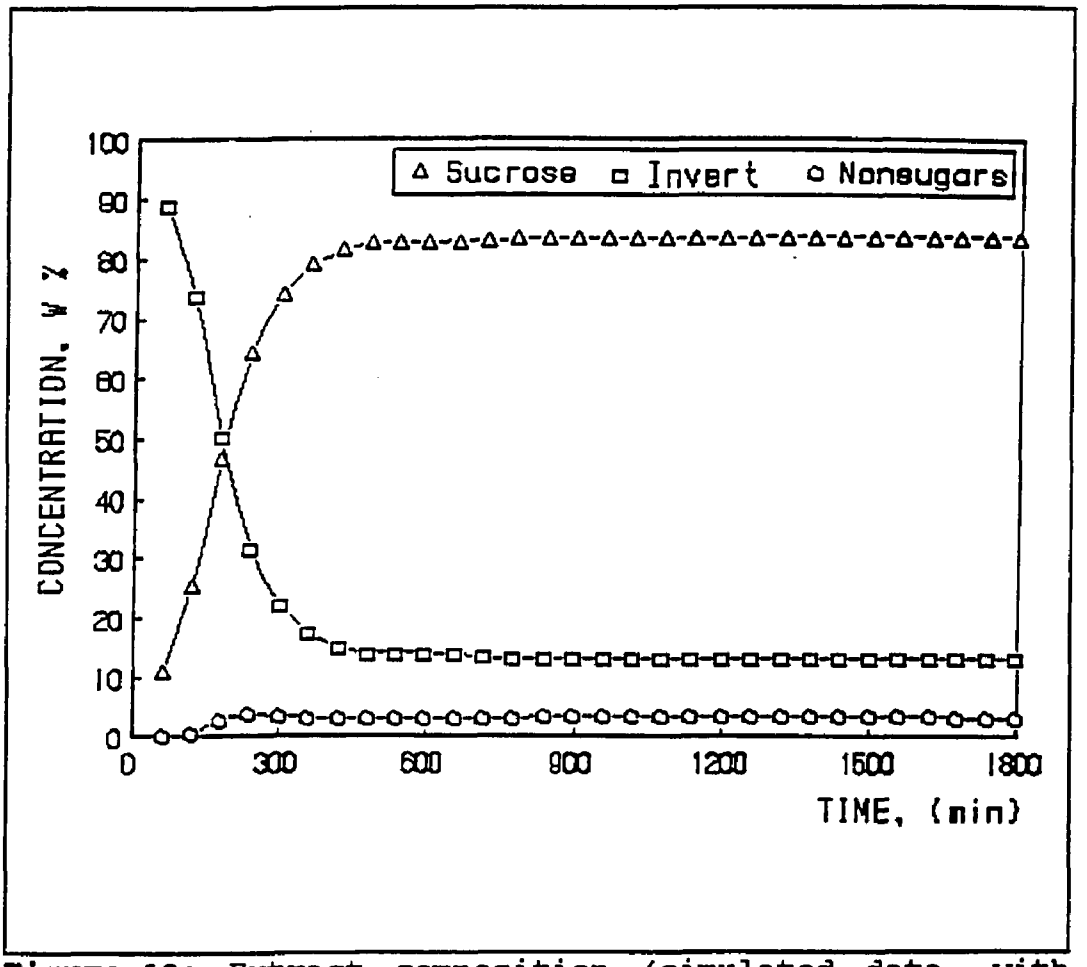

Figure 12: Extract composition (simulated data, with starting conditions as of Run #4)

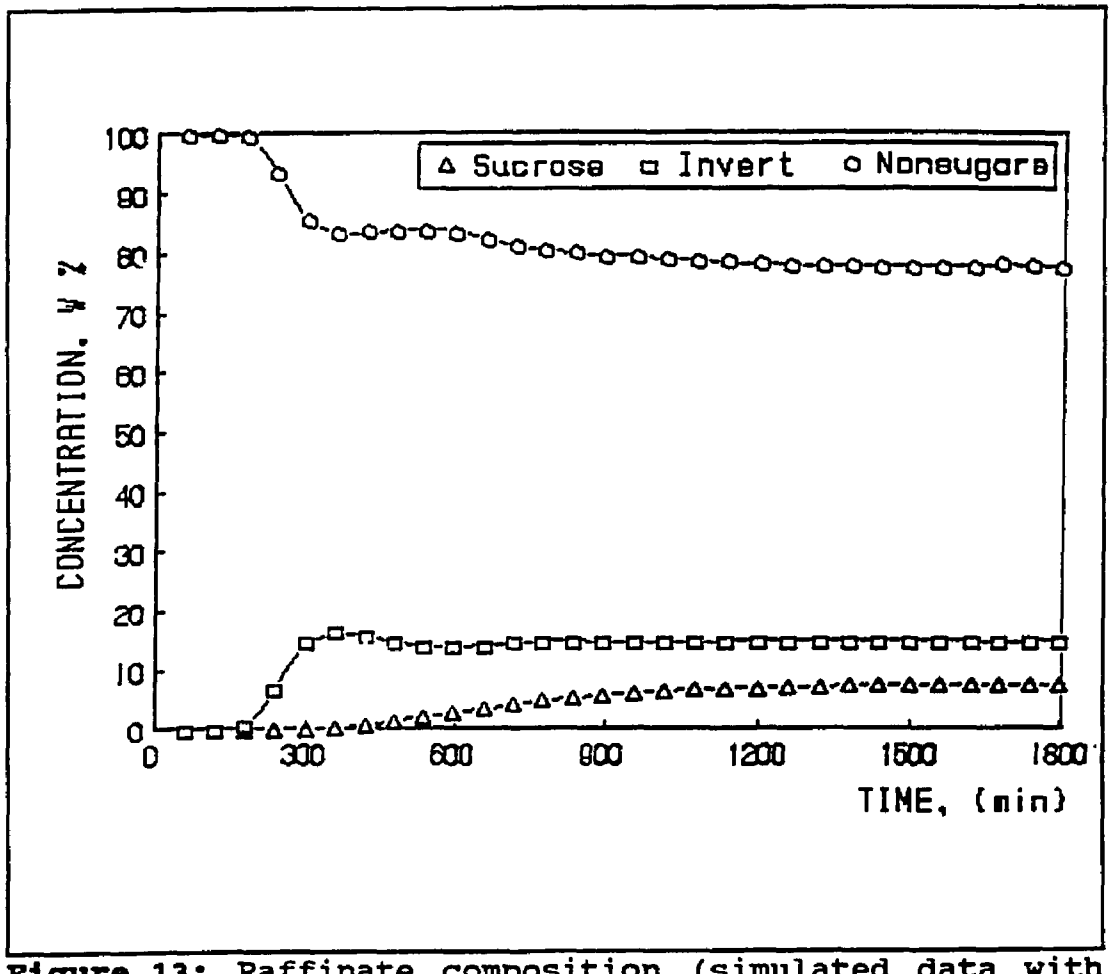

Figure 13: Raffinate composition (simulated data with starting conditions as of Run #4)

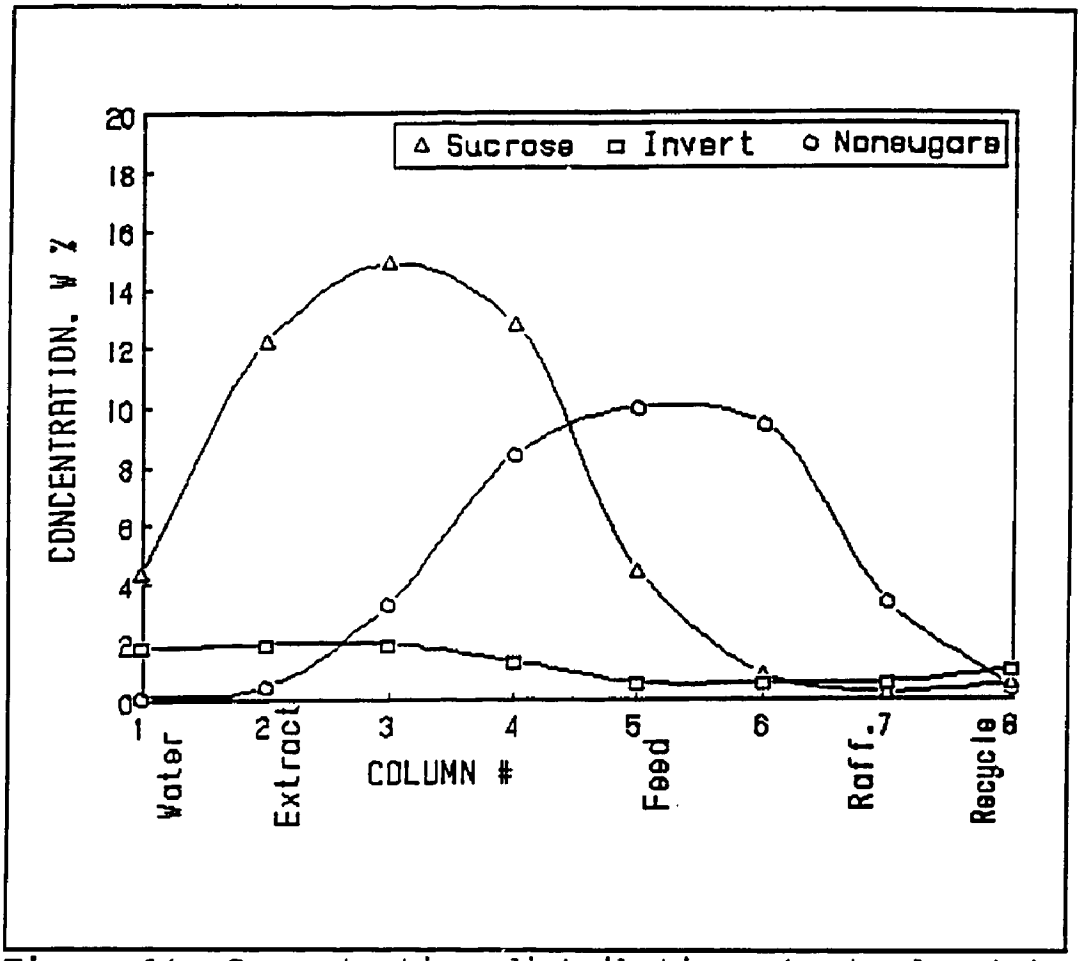

Figure 14: Concentration distribution at steady state (simulated data with starting conditins as of Run #4)

used to run the continuous experiments with molasses as feed.

4.2.3 Pre-treatment of Molasses.

To obtain a bright and clear molasses free of any suspended solids and with reduced hardness to be suitable for chromatographic system the following method was applied.

Phosphatation Treatment:

Lime and heat treatment for juice clarification is universally employed in raw sugar factories as it is an effective and economic process. This treatment results in heavy floccs, which adsorbs and entraps other non-sugar impurities which include gums, albumin and waxes of the juice. The composition of these flocculent is a mixture of $CaHPO_4$ and $Ca_3(PO_4)_2$ (Meade and Chen, 1977; Aguirre, 1982). It is evident that phosphate contents of the juice are responsible for an efficient clarification. Flocculent is added to juice after lime treatment to improve flocculation, settling rates and to reduce mud volume. Based on information from literature on desugarization of molasses (Schneider, 1978; Hongisto, 1979; Hongisto and Heikkila, 1978; Aguirre, 1982) and recognized effectiveness of phosphoric acid and phosphates as clarifying agents in sugar industry, it was decided that phosphoric acid will be used in pre-treatment of molasses to be separated on SMB ion exclusion plant. Pre-treatment of molasses scheme followed in this study is shown in Fig. 15.

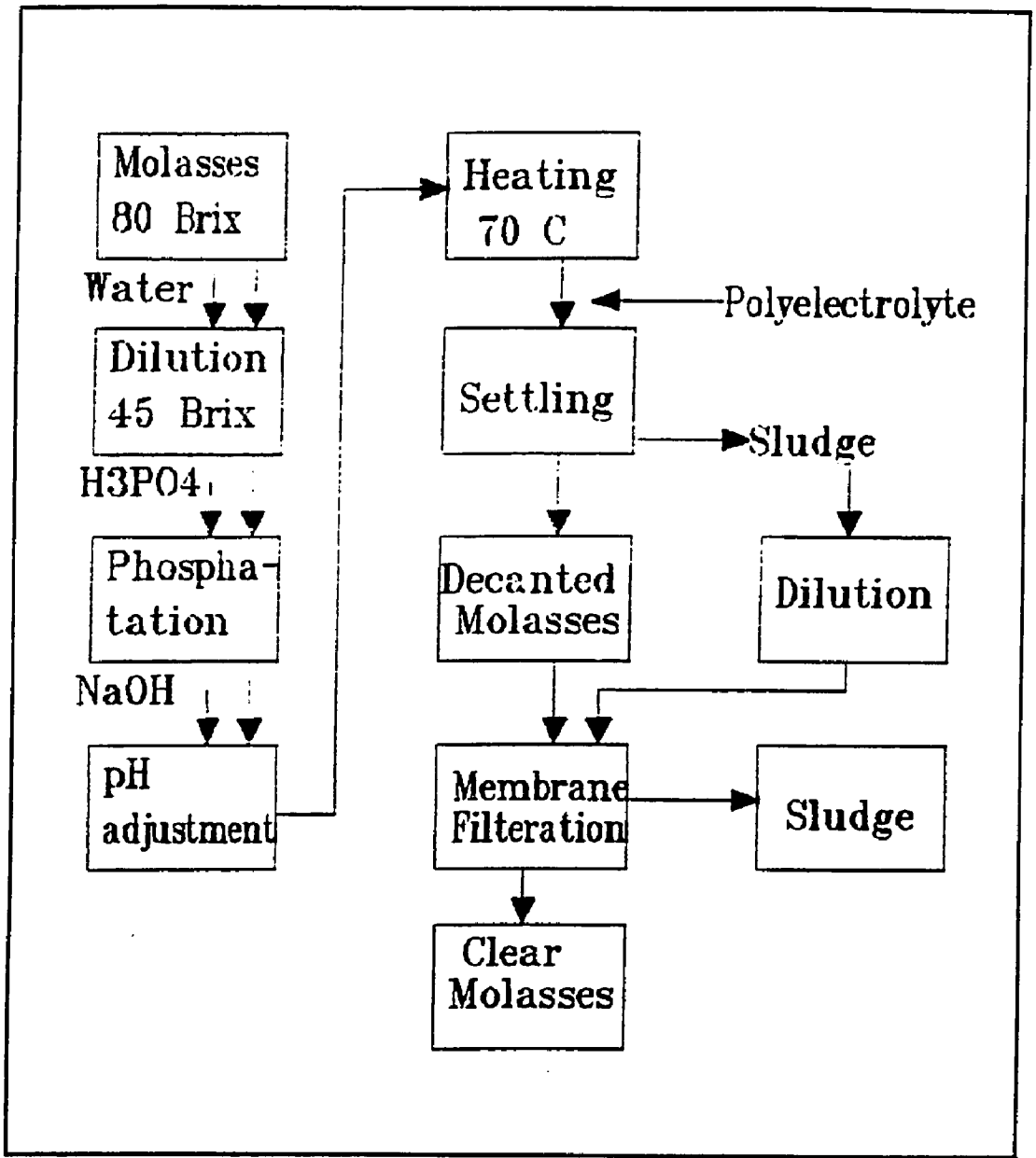

Figure 15: Pre-treatment of cane molasses by phosphatation and membrane filteration.

Elemental analysis:

Elemental analysis was used to have a basis of adding the amount of phosphoric acid to the molasses for decalcification purpose and at the same time to have the information about bivalent components of the feed.

For Runs #1 to #4, elemental analysis for Na, Ca, Mg, K, Fe, and Cu in molasses (and products) were conducted by Feed & Fertilizer Laboratory, Louisiana Department of Agriculture And Forestry, Agricultural Chemistry Division, LSU Campus, Baton Rouge by **Atomic Absorption** method. For Runs #5 & #6, **Standard EDTA Titration method** was adopted to analyze the total hardness as Ca/Mg (ppm Brix) of the molasses.

Experiment Runs #1 to #4.

Molasses were collected from different sugar mills in Louisiana in order to obtain representative molasses samples. Molasses were diluted to about 45 Brix by adding water. Phosphoric acid (98 %) was added at the level of 75 % of total hardness (Ca+Mg) of the molasses. This corresponds to about 120 % of Ca contents of the molasses. Molasses pH dropped to 4.4 by acidification. It was raised to about 7.2 to 7.5 by adding 10% NaOH solution. After that, Molasses were heated to 70 °C and filtered through the membrane filter. During filtration, temperature was maintained at 70 °C. Clear filtrate was separated. Sludge from filter was diluted and mixed with fresh molasses to

minimize the sugar losses. When the sludge was too viscous, it was discarded.

Experiment Run #5

Molasses were collected from Glenwood sugar mills. Phosphatation clarification of syrup is employed by this factory. Molasses were diluted to 25 Brix. Phosphoric Acid was added at the rate of 50 % of Ca contents. Molasses pH dropped to 5.3, but was adjusted by addition of NaOH (10%) solution to 7.8. After that, treated molasses were heated through tube heat exchanger to 80 °C and left in settling tanks after addition of poly electrolyte @ 3 ppm. After about 1 hour molasses were decanted from top. Sludge in the bottom was disposed off. Molasses were concentrated to 41 Brix by evaporating under vacuum.

Experiment Run #6

The same procedure for molasses as in Runs #1 to #4 was repeated with slight changes. Phosphoric acid used equivalent to 75% of total hardness (Ca^{++} + Mg^{++}). After neutralizing, molasses were heated to 80 °C and settled after addition of polyelectrolyte @ 3 ppm for about 75 minutes. The molasses from the settling tank were collected in two fractions: two thirds of the material was collected from the upper portion of the tank, and one third from the bottom of the tank. The latter fraction contained most of the settled mud. After filtration, the molasses were concentrated, under vacuum, to 60 Brix.

4.2.4 Continuous Experiments.

Parameters such as concentration of feed, flow rates of feed, water, recycle, extract and raffinate were selected from simulation data for continuous operation which based on the information from pulse testing. "LABTECH CONTROL" software was used for process control. Twelve channels were used in this program. First eight channels correspond to eight sequences. A sequence is an arrangement for opening/closing up of solenoid valves to introduce/extract different streams to and out of the system. Each channel controls twelve valves of the system in that particular sequence. These twelve valves include: one for molasses feed (in), one for water (in), seven valves for a flow in series, within the system columns, one valve for recycle flow through the pump, one for raffinate (out), and one for extract (out). After a pre-set time (switch time) the channel is moved into the next one and so on. The rest of the four channels were used to handle/store the data in the computer memory.

The system was heated to 70 °C temperature.

All four pumps were adjusted for selected flow rates.

Pre-treated molasses were heated to 50 °C.

The experiment can be started in any sequence by turning on the pumps and computer simultaneously. Position of process streams to and out of the system in different sequences are shown in Fig. 16. Feed enters the system at

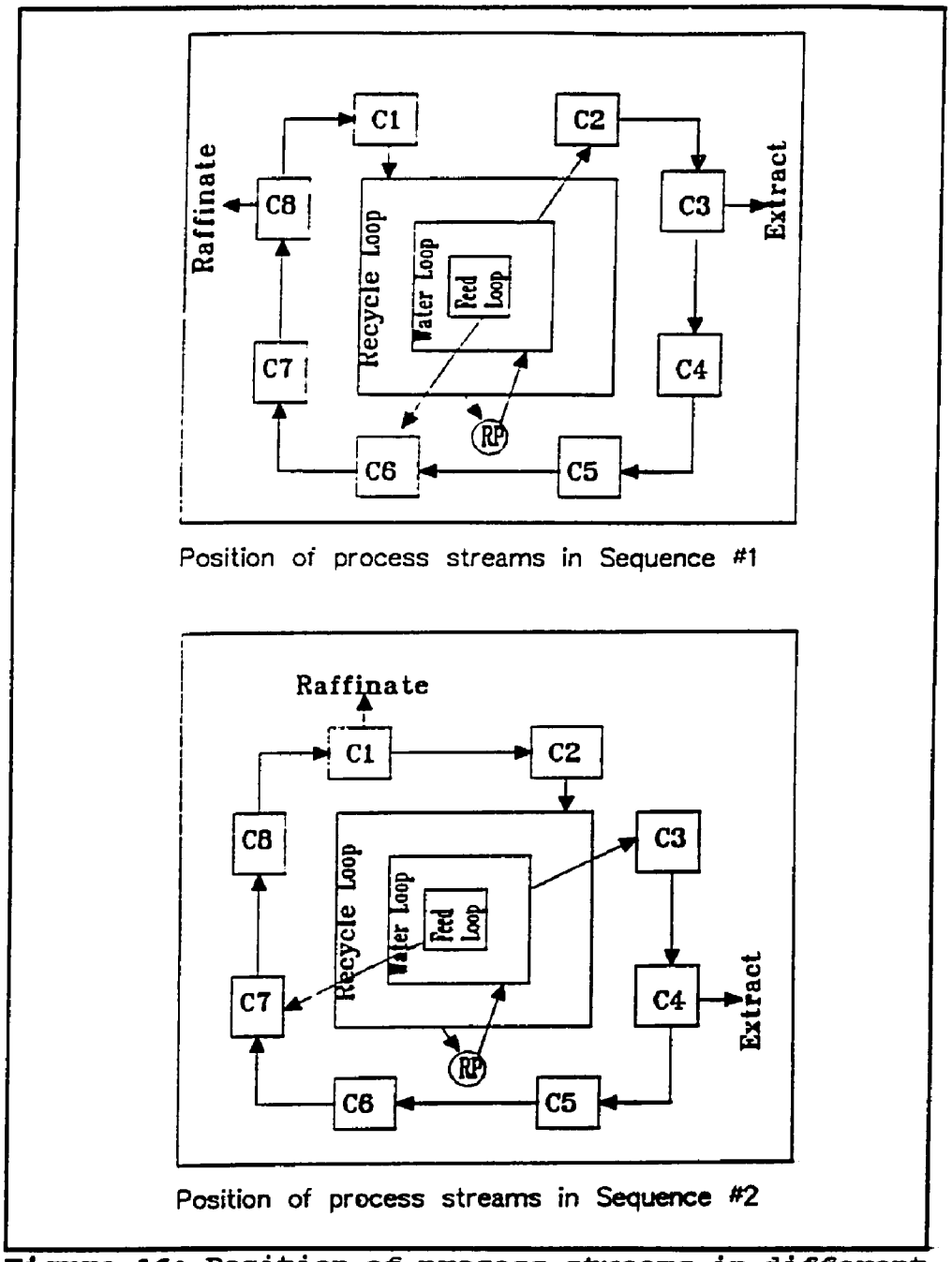

Figure 16: Position of process streams in different sequences of SMB operation.

a certain flow rate. At the same time, eluent water starts entering the system. Like pulse testing all flows were downward for the same reason. It takes about 4 to 5 hours to fill up the system with molasses by replacing the water already in the columns. Brix of the products was checked off-line. Products collection started from the very beginning of the experiment. Extract was collected on hourly basis and raffinate was collected on a half-hour basis in separate plastic bottles. After taking samples and weighing the mass, the products were moved immediately to freezer (10^0F). When the extract brix reached 1.0, HPLC analysis started for purity of extract and raffinate with emphasis upon the former. Sampling was done at mid-point of each switch time to have a representative sample. It is understood that if purity of extract is increasing, raffinate purity will be decreasing because of the law of mass balance.

By continuously monitoring the purity (sucrose contents) of the extract, separation operation was continued till extract purity drops sharply. When it dropped below a certain range, <70-75 in our case), then the experiment was stopped and samples from the bottom of each column were taken and analyzed by HPLC to have concentration distribution (Fig. 17) in the system. Based upon the "real" situation of the system, some corrective measures were adopted. These include moving back or forward in sequences,

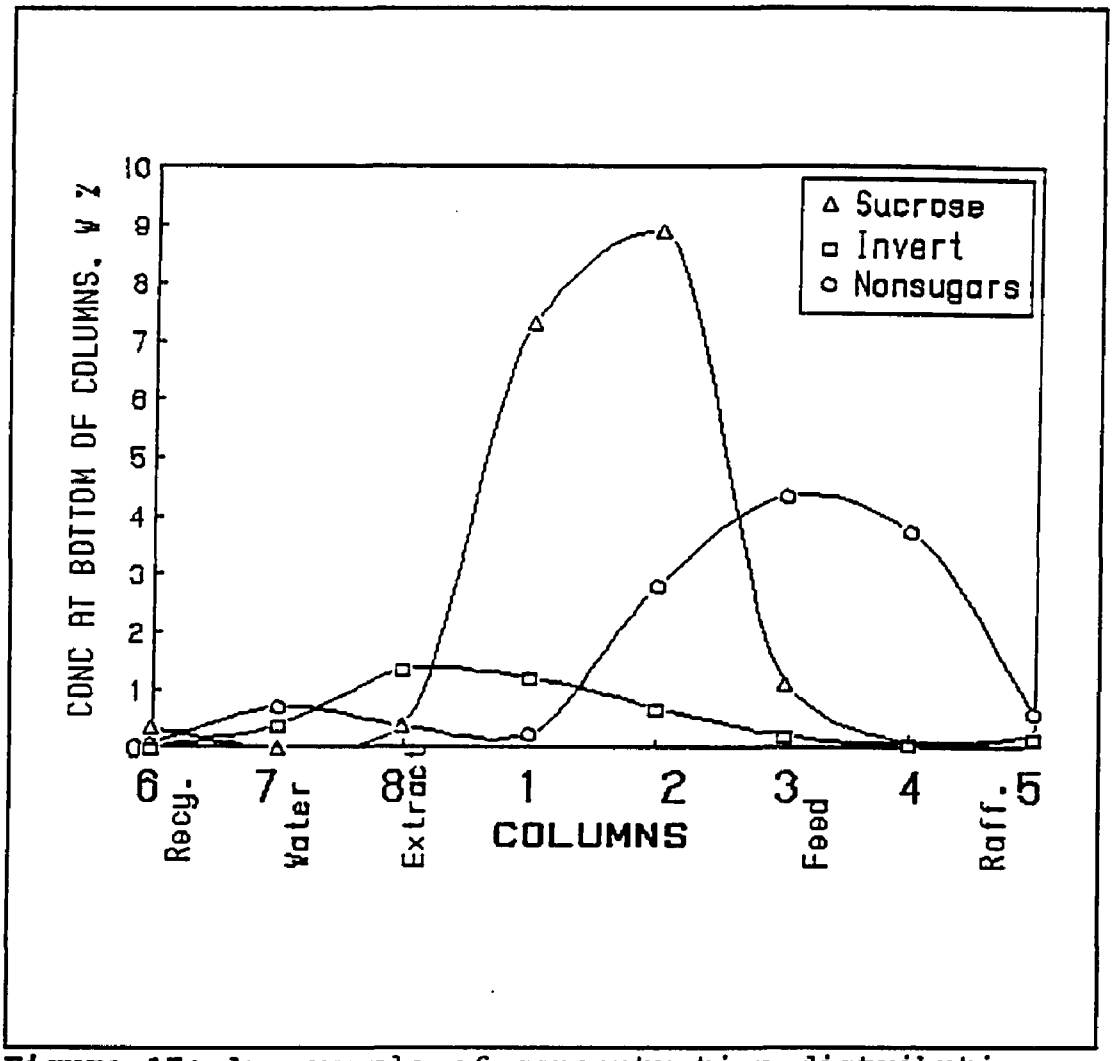

Figure 17: An example of concentration distribution on columns during the run. (Run #5; after 2.45 hrs; seq. #6, 1 min. elapsed)

depending how much system is off relative to expected situation. The other corrections include the change in flow rate of eluent, or of recycle. Again the experiment was started and separation was monitored in the same way.

Pre-treated and filtered molasses was used as feed for experiment Runs #1 to #4 and #6.

Molasses which was decalcified but not passed through the membrane filtration was also tried as filtration was a very complicated and time consuming operation with the equipment available. Only chemically treated molasses was used as feed for experiment Run #5. Experimental conditions at the start for all experiments are summarized in Table 8.

Table 8:
Experimental conditions at the start of the experiments Runs #1 to #6.

Experiments	Feed Bx	Feed Purity	Feed Flow Rate ml/min	Water Flow rate, ml/min	Extr. Flow rate, ml/min	Recyc. Flow rate, ml/min	Switch Time, min.
Run #1	40.5	43.7	20.0	120.0	30.0	218.0	8.6
Run #2	40.5	43.7	20.0	120.0	30.0	218.0	8.6
Run #3	40.5	43.7	20.0	120.0	30.0	50.0	18.0
Run #4	40.5	43.7	20.0	120.0	30.0	250.0	8.6
Run #5	41.0	51.2	20.0	120.0	30.0	280.0	8.6
Run #6	60.5	50.0	20.0	120.0	30.0	280.0	8.6

Note: Raffinate flow rate by difference = 20 + 120 - 30 = 110 ml/min

Resin Analysis:

Resin from the columns top was analyzed for K^+ ion concentration after Run #6. The detailed procedure is as provided by the manufacturer:

Took 25 ml resin by volume. Washed with 400 ml (deionized) water. Washed with 500 ml 5% HCl followed by 500 ml deionized water and collected the washing. Took 2.5 ml from this wash and diluted to 100 ml with water. Then concentration of K^+ was determined by Flame Photometer. Concentration of K^+ was calculated by the formula:

$$K^+ \text{ mg/ml of resin} = \frac{\text{Dilution x ppm (from graph)}}{\text{Volume of resin}}$$

4.2.5 Post-treatment.

Decolorization of Product Extract:

A combination of adsorbents (ADS 1/1) and ion exchange resins (XA100 1/1 and XA47 1/1) was used to accomplish this objective. A schematic figure of the setup of columns for decolorization is given in Fig. 10. Columns were packed with appropriate resin as described in Table 9.

Table 9:
Resin and bed volume used in decolorization of extract.

	Column 1	Column 2	Column 3	Column 4
Resin	ADS 1/1	XA100/1	ADS 1/1	XA 47/1
Volume	500 ml	1000 ml	500 ml	1000 ml

Extract (from Run #6) was passed through these columns separately (not in series as shown in Fig. 10). Four samples of 500 ml each, were collected after passing through each column and stored in refrigerator immediately. These samples were analyzed for brix, pH, and color.

Chapter 5

RESULTS AND DISCUSSION

5.1 Equilibrium Parameters.

5.1.1 Void Volume of the System.

For the Ca^{++} form resin, the void volume (ϵ) for the system was determined 0.47 (70 °C). This includes the column connection and valves etc.

For the K^{+} form resin, the void volume for the system at three various temperatures was found to be 0.40(30 °C), 0.39(50 °C), and 0.38(70 °C). This difference is because of the different degree of thermal expansion of the resin at different temperatures. At higher temperatures, the resin beads expanded more, these might change their shape from sphere to non-sphere because of some pressure by other particles, thus the ϵ of the system was reduced. There is another fact that when temperature is changed, it also effects the material of the column, glass in this case, which counters up to some extent the change in ϵ (Saska, 1992). Because of low thermal expansion value for the glass (8.3×10^{-5} / ^{0}C) this effect is not expected to be significant. Differences were observed in the void volume when determined separately for individual columns. Elution profiles of high M_w dextran 0.5% solution used to determine the ϵ of individual columns are shown in Fig. 18. ϵ varied

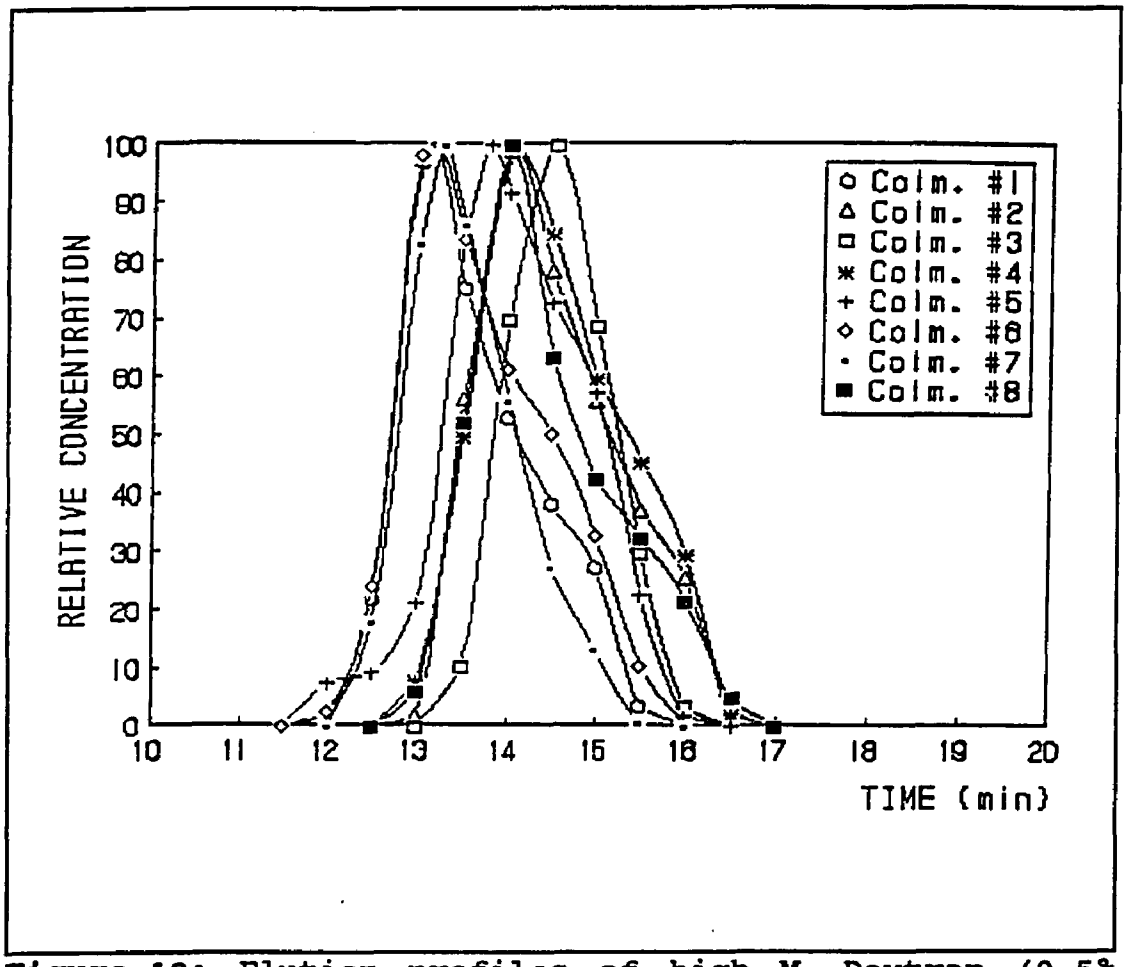

Figure 18: Elution profiles of high M_w Dextran (0.5% solution) on individual columns of SMB plant, packed with XUS 40166.00 resin. Feed 150 gms and Flow rate 157 ml/min.

between 0.348 and 0.386 depending on the column. These differences can be explained by the slightly different geometry of the individual columns and the differences in packing of the column. Top covers of some columns are smaller than the others,and thus hold different volumes of resin-free fluid, since resin cannot be filled beyond the neck of the column. This causes the differences in the shape of the peaks of the eluent of high molecular weight (M_w) dextran solutions used for the purpose.

The packing procedure of the columns also causes changes in the void volume. This leads to the difference in void volume for Ca^{++} form resin and K^+ resin. In the case of Ca^{++} resin, the resin was packed loosely as suspension of resin in water was poured in the columns till these were filled. Later, it was realized that this leads to excessive void space at the top of the column. It was more pronounced in the case of higher concentration solutions. Void space at the top of the column can cause back mixing in that region. In case of the K^+ resin, the packing procedure was changed. Resin was compacted by downward flow of KCl 10% solution through the columns, and more resin was filled in the void created. Columns were backwashed with water to remove any remaining KCl on the system. This procedure helped to reduce the void volume of the system to 0.41 (70 °C) in case of the K^+ form resin.

5.1.2 Dowex Monosphere 99 CA (Ca^{2+}) Resin.

The average HETP value for runs 1-4 and 7-10 was found to be 2.7 cm and 3.5 cm for glucose and fructose, respectively. These values are about one third of the values found by Ching and Ruthven (1984) on somewhat smaller columns. The experiments reported in the literature were performed on different resins, so some differences are expected in the findings.

The average values of the distribution coefficients are:

$$K_G = 2.45\text{x}10^{-1} + 5.1\text{x}10^{-3}\ C_G + 3.0\text{x}10^{-3}\ C_F$$

$$K_F = 4.70\text{x}10^{-1} + 7.0\text{x}10^{-3}\ C_G + 4.9\text{x}10^{-3}\ C_F$$

These values fall within the range reported in the literature for similar resins (Table 10). The separation judged by the ratio K_{F0}/K_{G0} is 1.92 in this study and is superior to that on the Duolite resin at the same temperature (Table 10).

Fructose forms a complex with Ca^{++} ions, due to the availability of properly spaced and oriented hydroxyl groups. Results of pulse testing on HFCS (30% W) shows that in case of fructose (Fig 19), the tail is made steeper because of the presence of glucose ($B_2 > 0$). That is why the broadening of the front is countered by the effect of the glucose.

Table 10:
Partition coefficient of Glucose (K_G) and Fructose (K_F) on several sulphonated polystyrene resins in Ca^{++} form.

Sorbent	Reference	T,°C	K_{Go}	A_1	B_1	K_{Fo}	A_2	B_2	K_{Fo}/K_{Go}
Dowex 50W-X8	Ghim and Chang, 1982	30	.30	0	0	.80	0	0	2.7
Zerolite 225 SRC 14	Ching and Ruthven, 1984	20 30 48 60	.20 .20 .20 .20	0 0 0 0	0 0 0 0	.78 .67 .56 .49	0 0 0 0	0 0 0 0	3.9 3.4 2.8 2.5
Duolite C204	Ching and Rythven, 1986	29 2.5 70	.50 .50 .50	0 0 0	0 0 0	.88 .75 .67	0 0 0	0 0 0	1.8 1.5 1.3
Korela V07C	Barker and Ganetsos, 1985		.215	0	0	.472	0	0	2.2
Duolite C204	Ching and Ruthven, 1985	25	.51	0	0	.88	0	0	1.7
Zerolite SRC14	Barker and Thawait, 1986 Ruthven, 1986	25	.126	.0039	.0024	.38	.0065	.00075	3.0
Duolite C204	Ching et al., 1987	55	.36	.001	.0015	.465	.0015	.0025	1.3
Duolite C204F	Viard and Lameloise, 1989	60	.374	0	0	.468	0	0	1.3
Dowex Monosphere 99 CA	This work	70	.245	.0051	.003	.47	.007	.0049	1.9

Note: a "0" indicate that this parameter was not determined (a linear model was assumed a priori) rather than that it was determined to be zero.

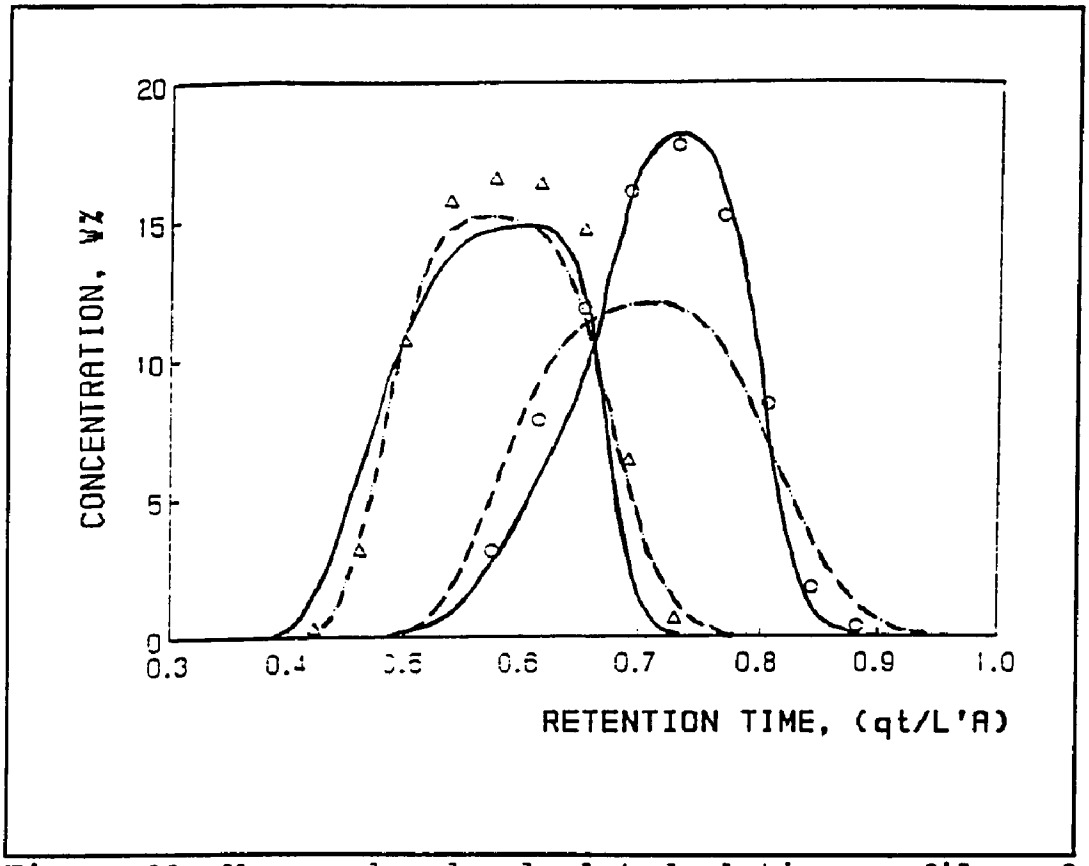

Figure 19: Measured and calculated elution profiles of glucose and fructose (Flow rate, 135 ml/min; feed 30 W% HFCS). solid line, non-linear model; dotted line, linear model; symbols, experimental data. Triangle, glucose; circle, fructose.

The non-linearity and coupling of the isotherms can be attributed to the limited accessibility of the internal surface of the resin for the sugar molecules. Because the median pore size of the resin and the diameter of the hydrated sugar molecule are of the approximately same size (≈10 Å), a large fraction of the pores becomes unaccessible for the sugar molecules. Though fructose has a higher affinity for the resin, the presence of glucose enhances the adsorption of fructose onto the resin beads. This probably leads to the displacement of hydration layers of counter ions and also of the diffusing sugar molecules to make some room to enter the pores of the resin beads. Also, at higher concentrations the contraction of the resin is expected (Mrini, 1991), so there is competition for the space available to diffuse into the bead through pores.

5.1.3 XUS-40166.00 (K^+) Resin.

Three different temperatures (30, 50, and 70 °C) and fluid velocities (5, 20 and 30 cm/min.) with two feed volumes (300 and 800 grams) were studied for the better understanding of the behavior of the major components of molasses under different conditions.

Effect of column loading.

It was found that adsorption of a component is a function of its concentration. It is very prominent in case of potassium chloride in this study. As the concentration increased, the potassium chloride peaks assumed a triangular

shape with a slow rising front and a sharp tail, but this was not the case for sucrose, as its peak remained Gaussian. This results from the fact that the rate of migration of solute i (KCl), which is a linear function of $\delta c_i/\delta q_i$, is higher for dilute solutions.

In spite of the fact that the retention time t ' and retention volume V ' increase with the column loading (Fig 20), sucrose, glucose, and fructose do not seem to be affected much by increased concentration as for as t ' and V ' are concerned. However, for potassium chloride, the behavior is somewhat different. At infinite dilution, V ' is about 0.39 ($\approx\epsilon$), while at loading of 12 g KCl per liter bed volume it increases to 0.58, indicating a steep rise. This is evident from curve 7 in Fig. 21 a & 21 b which corresponds to the maximum load (803 g of 14.4% KCl solution) in this study. Although the separation is still possible, the recovery of sucrose in sucrose-rich product will be reduced at higher concentration of salt (above 8 g/l) as the mass averaged retention time of potassium chloride is longer than that of sucrose. The trade off is reduced recovery. The curve S in Fig. 22 assumes independent behavior of potassium chloride and sucrose, as it was obtained by numerical integration of the elution profiles of potassium chloride (single component feed) at different loading, overlayed with those for sucrose at a single load of 65 g/l. For curve B, the calculation were

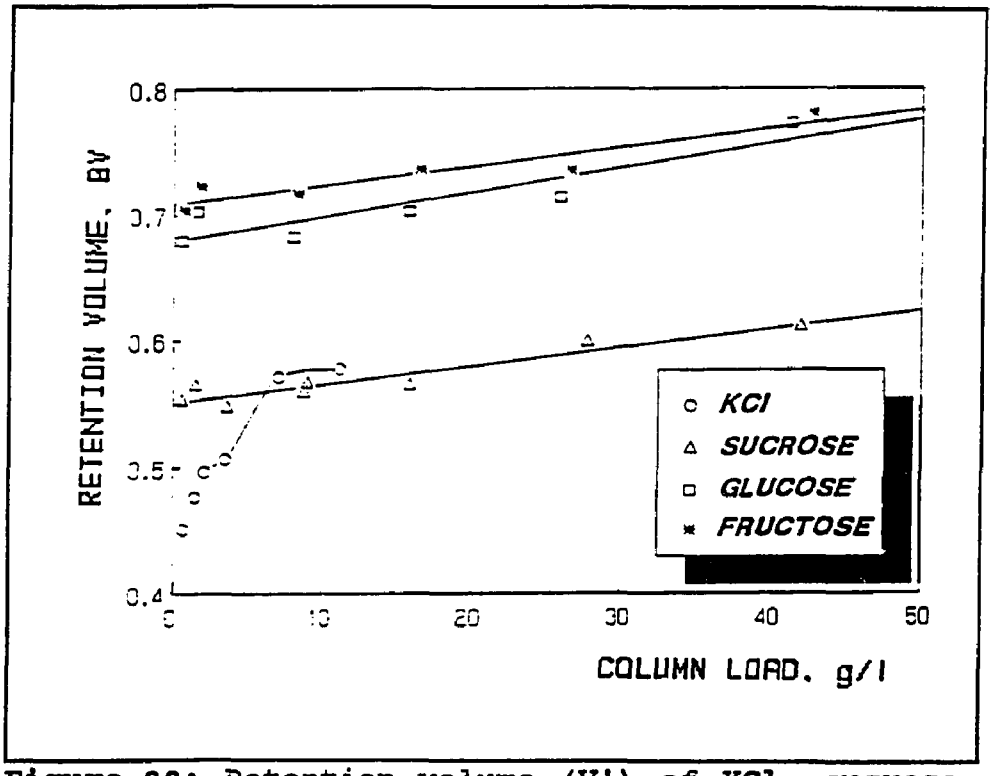

Figure 20: Retention volume (V') of KCl, sucrose, glucose, and fructose at various column loadings (Flow rate 150 ml/min. and 70 ^{0}C).

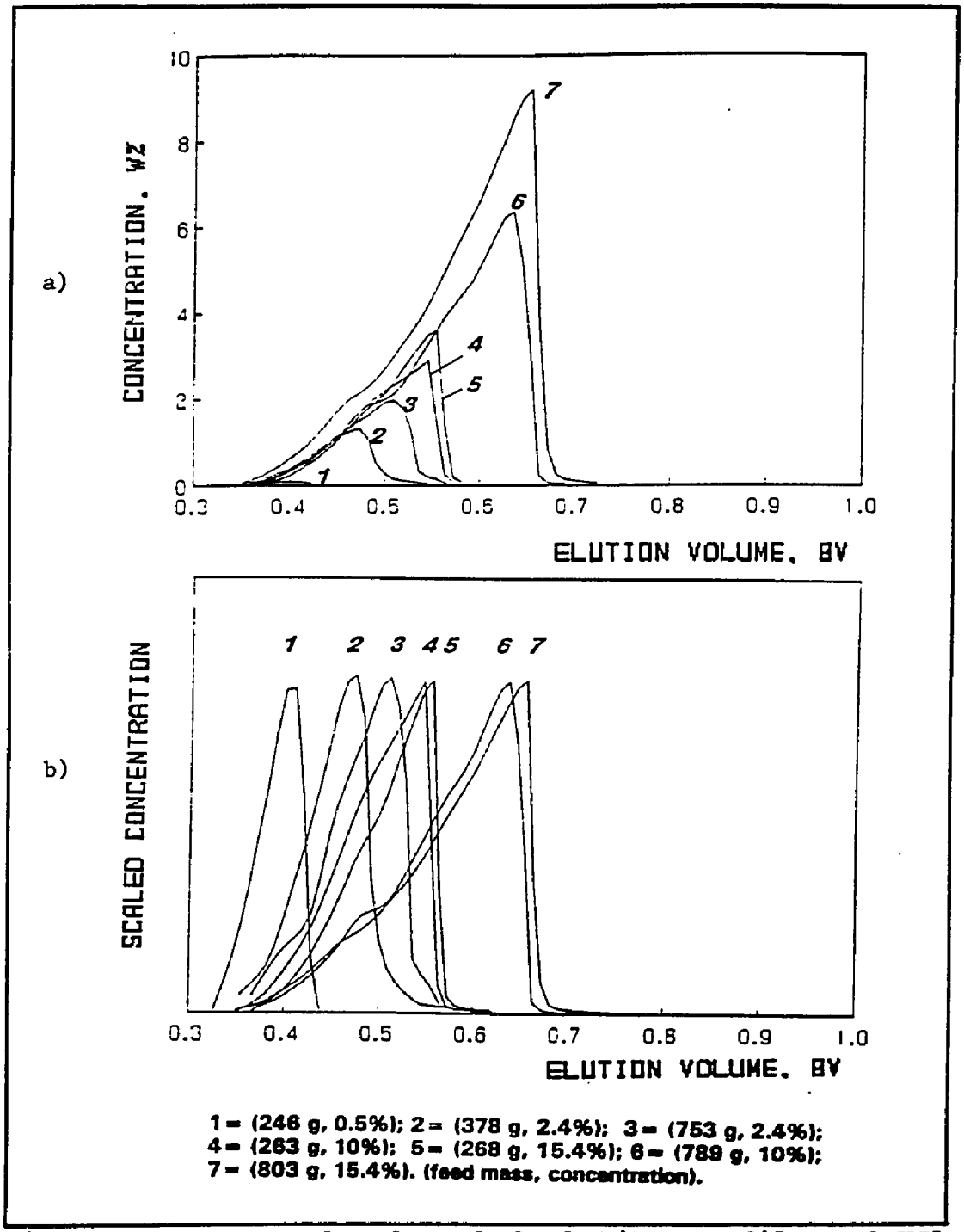

Figure 21: Measured and scaled elution profiles of KCl at various column loadings (Flow rate 150 ml/min. and 70 ^{0}C).

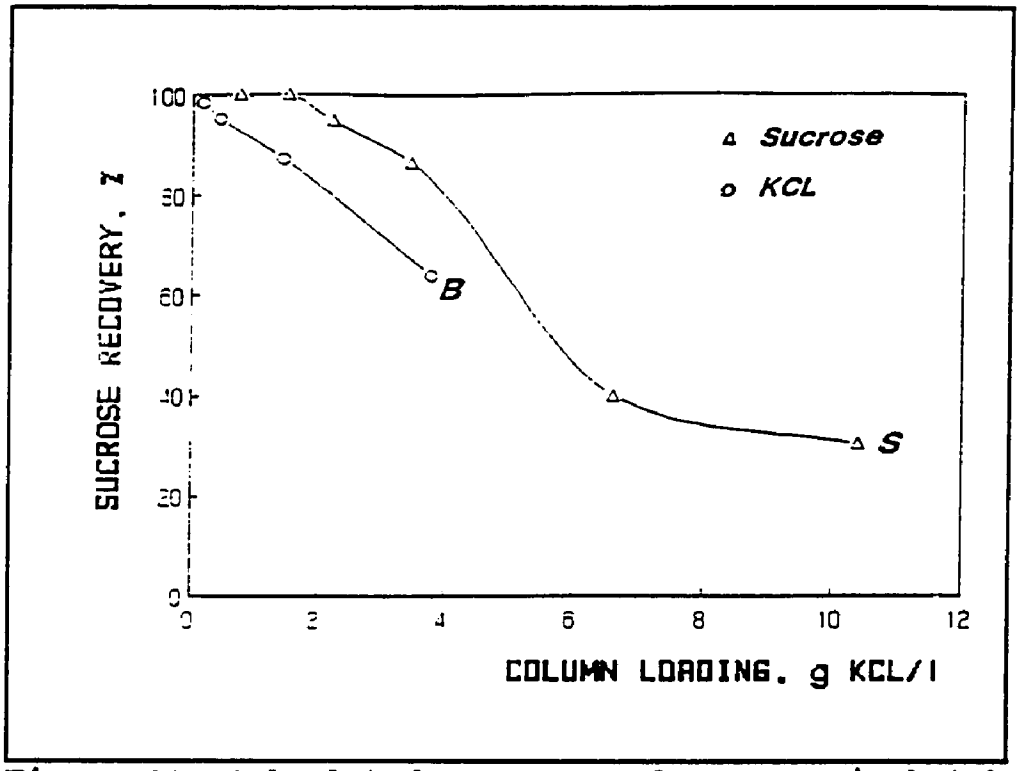

Figure 22: Calculated recovery of sucrose in batch chromatography experiments in the sucrose-rich product of 95% purity at various column loadings. B= binary feeds, 1:3 KCl/sucrose. S= calculated (from sucrose loading @ 65 g/l resin bed)

based on the profiles for 1:3 potassium chloride:sucrose solutions of different total concentrations.

Potassium chloride, sucrose, glucose and fructose were found to have K_{i0} values of 0.000, 0.215, 0.450 and 0.495, respectively. Potassium chloride is absent in resin at infinite dilution, but at higher concentration, its presence is observed by the comparative large magnitude of quadratic term. It is observed that sucrose/invert separation on K^+ resin is similar to glucose/fructose separation on Ca^{++} resin (Saska et al., 1991), with respective K_0 values of 0.245 and 0.47. The curvatures of the isotherms for the three sugars are small and nearly identical, with an average curvature (measure of departure from linearity) of 0.004. This value can be compared to the self and cross coefficients determined for glucose and fructose on Ca^{++} resin. Thus it can be assumed that the non-linearities of the respective isotherms are because of such a mechanism which is similar for the sugars under consideration, and it is not affected by the ionic form of the resin. However, it must be noted that there is a large uncertainty in the cross-coefficients for the potassium chloride/sucrose mixtures.

Potasium chloride and sucrose interaction resulting in an enhanced adsorption. This leads to a slower front for the slower component, sucrose in this case, and making the peak taller and narrower (Fig 23) than it would be if the behavior of the component was independent of each other.

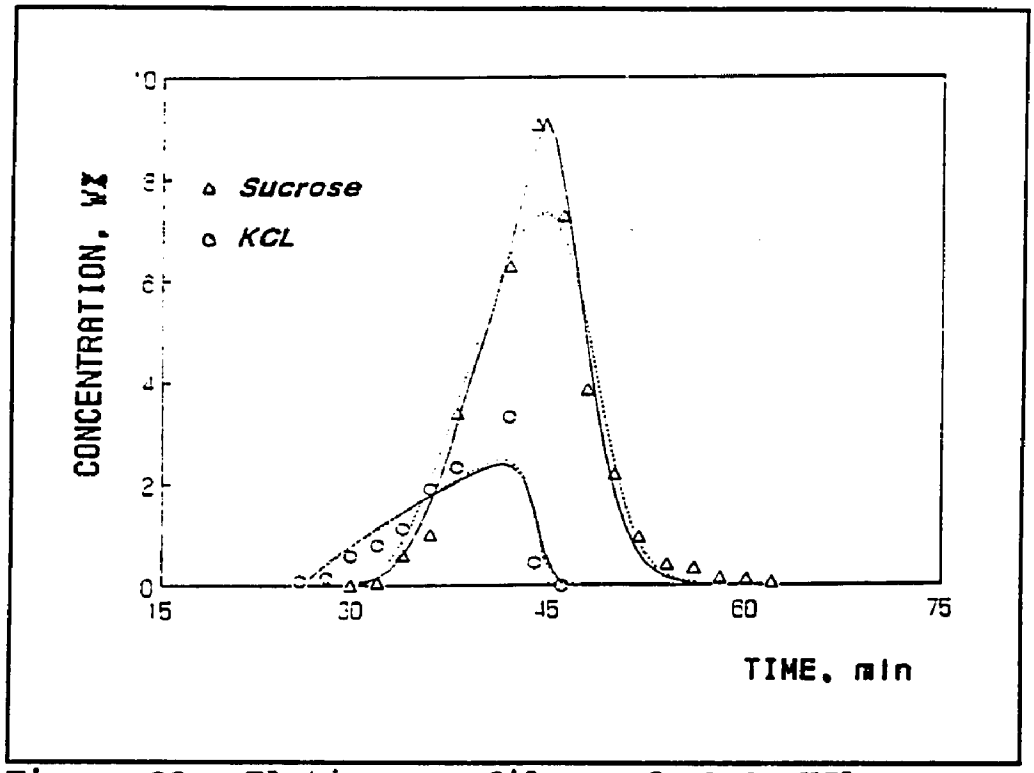

Figure 23: Elution profiles of 1:3 KCl:sucrose mixture (feed 791 g; 25% solution; flow rate 150 ml/min.; 70 ^{0}C) Calculated as non-linear model. Uncoupled isotherm, dotted line; coupled isotherm, solid line.

This is similar to the observations for glucose/fructose mixture. However, this appears to contradict the results obtained by Meyer et al.(1965) in the experiment on DOWEX 50W X4 (K^+) in which at 90 ^{0}C an increase in solution concentration of potasium chloride was found to decrease sucrose adsorption. They also concluded that adsorption isotherm for potassium chloride was quadratic and increasing liquid concentrations of sucrose resulted in an increased potasium chloride adsorption, which supports the observations in this work.

Table 11:
Parameters of the adsorption isotherms determined on XUS-40166.00 resin. (when i = sucrose then j= potassium chloride)
Assumed form of $K_i \equiv q_i/c_i = K_{i0} + A_i c_i + B_i c_j$

i	T,^{0}C	K_{i0}	A_i	B_i (#)
KCl	70	.000	.064 (.016, 6)	.026 (.038, 12)
	50	.013	-	-
	30	.033	-	-
sucrose	70	.215	.004 (.001, 6)	.018 (.013, 8)
	50	.223	-	-
	30	.235	-	-
glucose	70	.450	.004 (.002, 5)	-
fructose	70	.495	.003 (.002, 5)	-

(#) B_i was determined only for 1:3 Potassium chloride: sucrose mixture at total concn. from 3 to 40 % and two feed volumes of 300 and 800 ml. The numbers in parenthesis are the std. deviation and the numbers of experimental points, respectively.

<u>Effect of flow rate and temperature.</u>

Flow rates within the column are one of the most important parameters for an SMB operation. These are used for optimizing the separation by varying within certain

limits. It was important to know how the behavior of major components of the molasses is affected by the flow rate. It is generally recognized that by increasing flow rate, HETP is increased which causes an overlapping of peaks leading to a poor separation.

Retention times and HETP for potasium chloride and sucrose at infinite dilution at the three temperatures were determined at different flow rates (Fig 24 & 25). To have information about the behavior of sucrose at conditions (≈60 brix, 70 ^{0}C), closer to industrial ones, were also studied. It was observed that fluid velocity has no significant effect on retention time for potasium chloride but in case of sucrose it was found to be a function of fluid velocity. The same effect was observed for sucrose at lower temperatures. This phenomena can be explained as at higher fluid velocities, the sucrose molecules do not get enough time to diffuse inside the resin (thus equilibrium stage is not reached) and it travels at faster rate relative to than if it would at lower liquid velocities. Decrease in retention time for sucrose at lower temperature is more pronounced as the diffusion coefficient of sucrose becomes smaller at lower temperatures.

Pulse Testing on XUS-40166.00 (K^{+}) resin with sugarcane molasses.

Non-sugars of sugarcane molasses consist not only of inorganic and salts but also includes colorants,

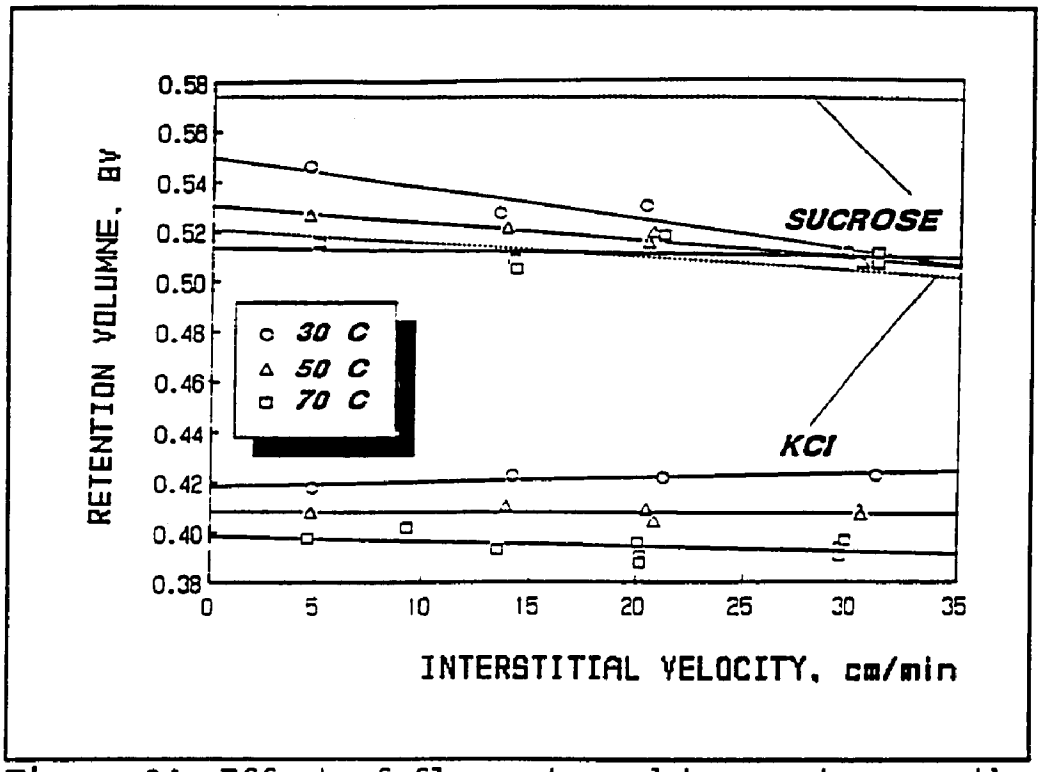

Figure 24: Effect of flow rate and temperature on the retention volume (V') of sucrose and KCl (single component feed) at infinite dilution (300 g of 0.5% concentration), and high concentration (300 g, 61% and 15% for sucrose and KCl respectively).

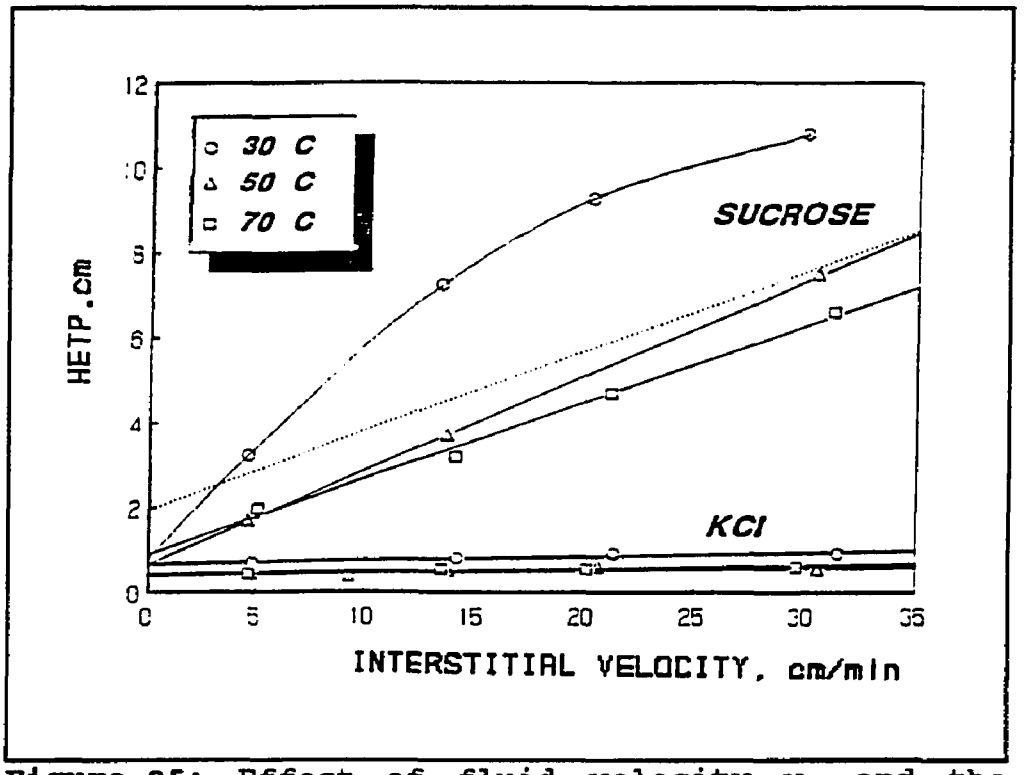

Figure 25: Effect of fluid velocity v, and the temperature on the HETP. Experimental data at infinite dilution. solid line; experimental data of sucrose at high concn.(300 g of 61% concn. at 70 ^{0}C).

polysaccharides, etc. For a reliable design for SMB operation, all the components of non-sugar fraction of the molasses must be taken into account. It was observed that when non-sugars are considered as potassium chloride, and K_{KCl} was used as K_{NS} (= 0.064), the expected non-sugars band was slower than the experimental one (Fig 26a). However, when non-sugars were considered as non-retained components ($\Rightarrow K_{NS}$ = 0), the expected non-sugar band is faster than the experimental one (Fig 26b). It can be assumed that actual behavior of non-sugars is somewhere between those of potassium chloride and non-retained components, it is evident from Fig 26c , when the molasses were considered as a mixture of five components, i.e. sucrose, glucose, fructose, 50% non-sugars with K = 0, and 50% non-sugars with K = K_{KCl}, the calculated data was better fit to the experimental data. Thus it will be fair to assume a part of non-sugars as non-retained components and a part as potasium chloride for modeling purpose.

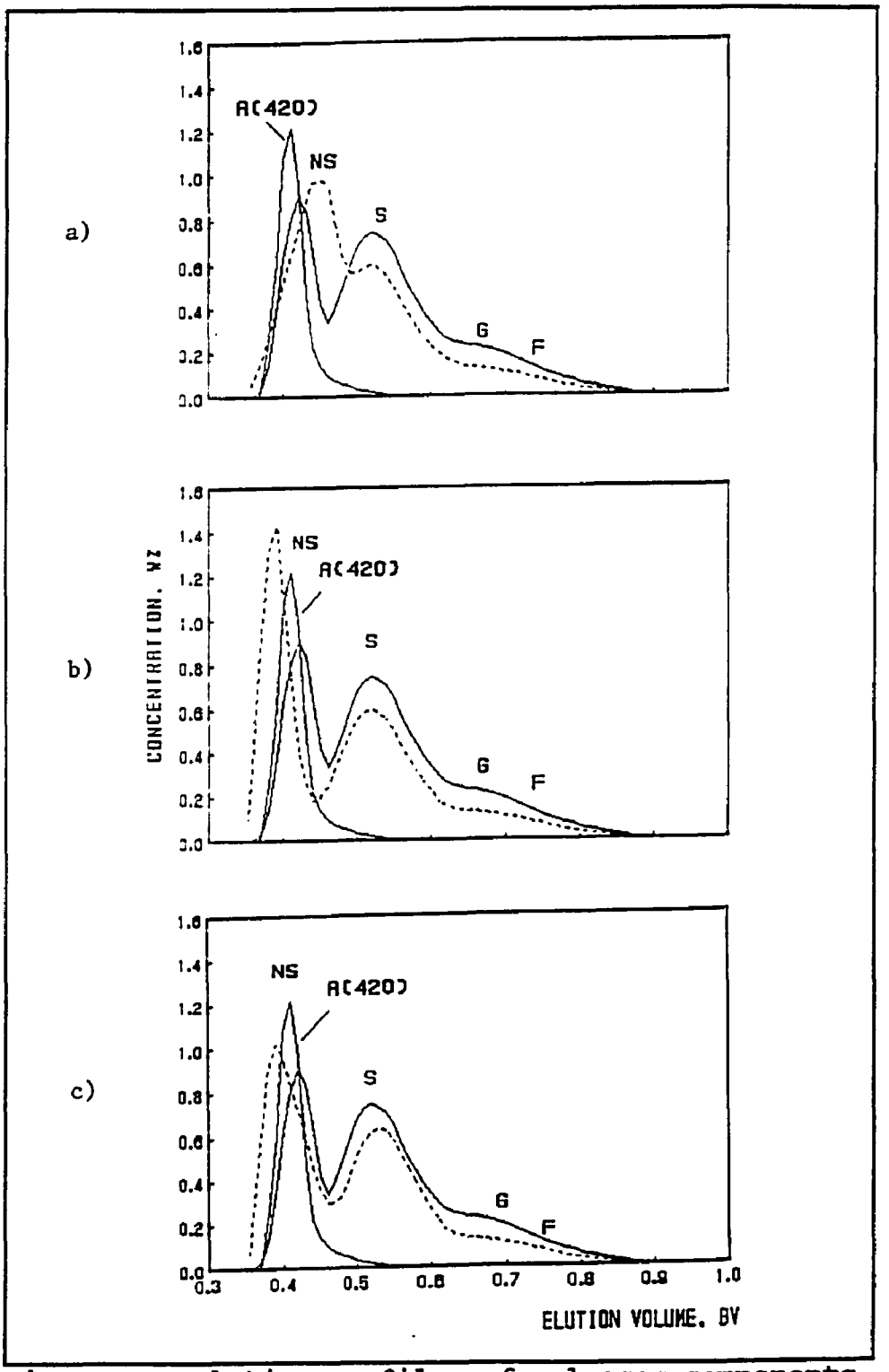

Figure 26: Elution profiles of molasses components. Experimental (solid line) and calculated (dotted line) as a) Non-sugars =K ≡ 0, b) Non-sugars =K ≡ 0.064 c, and c) Non-sugars, 50% = K ≡ 0, 50% = K ≡ 0.064 c.

Table 12:
Conditions of glucose solution used for pulse testing on DOWEX 99 Monosphere Ca^{++} resin.

Experiment	Feed Concntration, Brix	Feed Mass (Dry) gm
Run 1	11.0	33.0
Run 2	20.5	62.5
Run 3	30.4	96.7
Run 4	60.5	219.0
Run 5	16.8	668.0
Run 6	20.0	1603.0

Table 13:
Conditions of fructose solution used for pulse testing on DOWEX 99 Monosphere Ca^{++} resin.

Experiment	Feed Concntration, Brix	Feed Mass (Dry) gm
Run 7	10.0	30.0
Run 8	20.4	62.6
Run 9	29.7	95.0
Run 10	59.7	218.0
Run 11	20.0	905.0
Run 12	20.0	1814.0

Table 14:
Conditions of high fructose corn syrup (HFCS) used for pulse testing on Dowex 99 monosphere Ca^{++} resin.

Experiment	Feed Concentration, Brix	Feed Mass (Dry) gm
Run 13	10.0	583.0
Run 14	20.0	1147.0
Run 15	30.0	1844.0
Run 16	41.0	2605.0
Run 17	60.0	4187.0

Note: The feed mass given is mass of component in the total volume of the solution fed.

5.2 Continuous Experiments.

Six separate experiments were performed to optimize the separation performance of Simulated Moving Bed (SMB) Ion Exclusion System, on a pilot plant scale. The performance of SMB as reported in the literature is affected primarily by the flow rates in the system, column loading, feed purity, and feed hardness. The results of these experiments are presented in the Tables 15 & 16. These experiments are designated as Run #1 to Run #6. Feeds are designated as Feed 1, Feed 2, and Feed 3 for Runs #1 to #4, Run #5, and Run #6, respectively.

Molasses History:

The molasses conditions for all these experiments were as follows:

a. Molasses for Runs #1 to #4 were collected from 12 different Louisiana sugar mills from crop 1990. The molasses for Run #5 were collected from Glenwood sugar mill, of crop 1990. The molasses for Run #6 were collected from Cinclare sugar mill of crop 1991.

b. Molasses for Run #1 to Run #4 and for Run #6 were decalcified and filtered through vortex flow filtration (V.F.F.) unit as described in material and method. For Run #5, molasses were decalcified and decanted after settling for about one hour. No V.F.F. treatment was applied.

Table 15:
Results of continuous experiments with cane molasses on SMB pilot plant.
(Product: Extract)

Experiment	Brix	Color I.U.	Composition % on solids				% Recovery			
			Suc.	Inv.	Sal.	Sug.	Suc.	Inv.	Sal.	Sug.
Run #1	11.8	35690	43.5	8.7	47.8	52.2	82.5	57.1	10.0	76.7
Run #2	9.8	26577	78.0	10.7	11.3	88.7	87.1	42.9	17.0	77.7
Run #3	7.9	17802	75.4	15.7	8.9	91.1	98.5	69.6	25.3	91.8
Run #4	13.9	16900	81.0	15.0	4.0	96.0	86.5	52.5	4.1	78.5
Run #5	14.5	35172	81.0	11.9	7.2	92.7	75.5	37.7	9.8	67.1
Run #6	21.9	30550	80.3	15.5	4.2	95.8	88.1	39.8	6.5	78.9

(Suc. = Sucrose; Inv. = Invert; Sal. =Non-sugars; Sug. =Total Sugars)

Table 16:
Results of continuous experiments with cane molasses on SMB pilot plant.
(Product: Raffinate)

Experiment	Brix	Color I.U.	Composition % on solids				% Recovery			
			Suc.	Inv.	Sal.	Sug.	Suc.	Inv.	Sal.	Sug.
Run #1	2.9	56075	63.8	17.0	19.2	80.8	17.5	42.9	90.0	23.3
Run #2	2.3	119716	14.3	16.4	69.3	30.7	12.9	57.1	83.0	22.3
Run #3	0.8	154870	3.4	19.9	76.6	23.5	1.5	30.4	74.7	8.2
Run #4	4.1	82300	10.5	11.2	78.3	21.7	13.5	47.5	95.9	21.5
Run #5	4.5	165000	23.2	17.6	59.2	40.8	24.5	62.3	90.2	32.9
Run #6	6.1	112500	11.5	24.7	63.8	36.2	11.9	60.2	93.6	21.1

(Suc. = Sucrose; Inv. = Invert; Sal. = Non-sugars; Sug. = Total Sugars).

c. For Runs #1 to #4 feed molasses concentration was the same i.e. 40.5 Bx and concentration of feed molasses for Run #5 was 0.5 degree more. For Run #6, feed molasses concentration was 60.5 Bx.

The composition of molasses used in these experiments is given in Table 17.

Table 17:
Composition of feed molasses. (on solids)

Experiment	Sucr. %	Inv. %	Salts %	Hardness Ca/Mg ppm(Bx)	Colorants I.U.
Runs #1-#4	43.7	13.2	43.1	2840	75850
Run #5	51.2	14.5	34.3	2810	97348
Run #6	50.0	21.1	28.9	2520	79845

Starting/Running conditions:

Starting conditions for the experiments which include flow rates of feed, water, extract, raffinate, and recycle and switch time from one column to another in the system, were selected from the simulated data calculated based on the conditions of the experiments (Figs. 11-14). The best switch time and flow rates selected and tried for real experiments are shown in Table 8.

The flow rates and switch time were changed in the course of the experiments to achieve an optimum separation between sugars and nonsugars. The details of changes made are given in Appendices A1 to A6.

For each experiment, the extract and raffinate samples were analyzed on the run by HPLC for sucrose, invert and salts (including all non sugars) concentration. The purpose was to monitor the operation for a good separation between sugars and non-sugars. These data is given in Appendices B1 to B6.

A purity of 75 in the extract was selected as a basis of good separation, if purity of extract dropped below this figure, then the experiment was stopped and some corrective measures were taken to improve the separation while continuing the experiment. The run time for each experiment and the reason of termination are summarized in Table 18.

For each experiment, material balance (Appendices C1 to C6) was made to find the recovery of various components in the products to evaluate the performance of the system.

Table 18:
Run time of experiments.

Experiment	Run Time, hrs	Reason for termination.
Run #1	9.11	Good separation no longer expected.
Run #2	11.20	Data collection completed and no significant changes expected.
Run #3	9.16	Good separation no longer expected.
Run #4	24.90	Run out of feed molasses.
Run #5	36.71	High working pressure.
Run #6	28.58	Data collection completed and no significant changes expected.

5.2.1 Pre-treatment.

Hardness/Suspended Solids:

Molasses as feed for the chromatographic system needs to be 'cleaned-up' to remove suspended solids and to minimize the divalent ions such as Ca^{2+} and Mg^{2+}. This objective was accomplished by the modified procedure as described in the material & methods (sec.4.3.3).

Removal of the divalent ions was emphasized as these have significant effect on the separation efficiency of the chromatographic system (sec. 2.4.3). Other inorganic constituents such as K, Na, P, Fe, and Cu were analyzed for in molasses after clarification (Feed 1) and molasses before treatment (used as Feed 2 after clarification), and for composite products obtained from Runs #1 through #4. Although these are not expected to have a significant effect on the separation but the effect of pre-treatment on their concentration was studied (Table 19). An increase in percentage of phosphate and sodium observed in the treated molasses may be attributed to the addition of H_3PO_4 and NaOH which were used to precipitate the suspended/soluble solids and neutralize the pH of the molasses respectively. However, the observed percentage increase in Cu can not be explained and may be due to certain impurities or may be due to certain interactions of certain unknown impurities and contaminants present in the molasses. No significant

changes in the concentration of K was observed due to the treatment of molasses by H_3PO_4 and NaOH.

Total hardness of molasses was measured as sum of Ca and Mg (Ca/Mg). Results of pretreatment are shown in Table 20. It was observed that phosphatation treatment (followed by vortex flow filtration in case of Feeds 1 and 3) resulted in a decrease of total hardness by a factor of 3.7 (2500-2800 ppm).

The hardness of the molasses after pre-treatment is rather high when compared with (500-1000), reported in the literature (Gadomski, 1991; Kakihana, 1989). It can be related to the fact that composition of molasses vary within a wide range (Clarke and Godshall, 1987), so no specific figures can be described as standard in such a case. However, it will be discussed later whether this range of hardness had any adverse affect on the separation and quality of the products of the SMB system.

Table 19:
Inorganic constituents of cane molasses (other than Ca/Mg) on solids.

Molasses	K %	Na %	P %	Fe ppm	Cu ppm
Feed 2′	5.54	0.18	0.10	247	13
Feed 1	5.45	2.04	0.27	66	16

 # before treatment.

Table 20:
Hardness as Ca/Mg (ppm on solids) in cane molasses used in SMB operation.

Molasses	Before treatment	After treatment
Feed 1	9500	2840
Feed 2	8780	2810
Feed 3	9110	2520

Color:

Pre-treatment reduced the colorants of molasses by factors in the range of 2.50 and 2.15. The lower color reduction was for molasses not treated by V.F.F. (Table 21).

Table 21:
Color of molasses.

Molasses	Before Treatment	After Treatment
Feed 1	2.10×10^5 I.U.	7.6×10^4 I.U.
Feed 2	1.90×10^5 I.U.	9.7×10^4 I.U.
Feed 3	1.95×10^5 I.U.	7.9×10^4 I.U.

The V.F.F. treatment may be significant since the membrane involved may exclude some very high molecular weight colorants. Some of the low molecular weight colorants which can not be expected to be removed with V.F.F. process can be adsorbed by the resin, which result in more inclusion with sugars in the extract.

Molasses were observed to be bright and clear of any suspended material after the complete pre-treatment process. No information about reduction of colorants in pre-treatment of molasses is available in the literature. However, it has been reported that a syrup clarification with phosphoric

acid and lime removes about 10% of the soluble color (Clarke and Godshall, 1987). Thus it is evident that pretreatment with phosphoric acid followed by V.F.F. can be effective in removal of color of the molasses.

5.2.2 Separation.

Experiment Run #1.

The total concentration as Brix, and concentration of sucrose, invert, non-sugars of extract and raffinate for this run is shown in Figs. 27 to 32. The purity (sucrose) of the extract dropped below 75 after about two and half hours (Fig 27). On the other hand the purity of raffinate which was very low in the beginning of the experiment, had risen and exceeded the purity of feed molasses. The situation could not be improved despite various corrective action were tried. The main reason was the improper flow of fluids in the different zones of the system, which pushed the sucrose (and invert) towards the raffinate outlet rather towards the extract outlet. This situation was worsened by untimely corrective actions and led to an "inverse separation". The reason for untimely actions was that in this experiment, the analysis arrangement was such that there was a delay of about 30 minutes in getting results of the sample analyzed. The experiment had to be stopped because it was realized that no improvement was possible under the existing conditions. The average composition of the extract and raffinate for this run is given in Table 22.

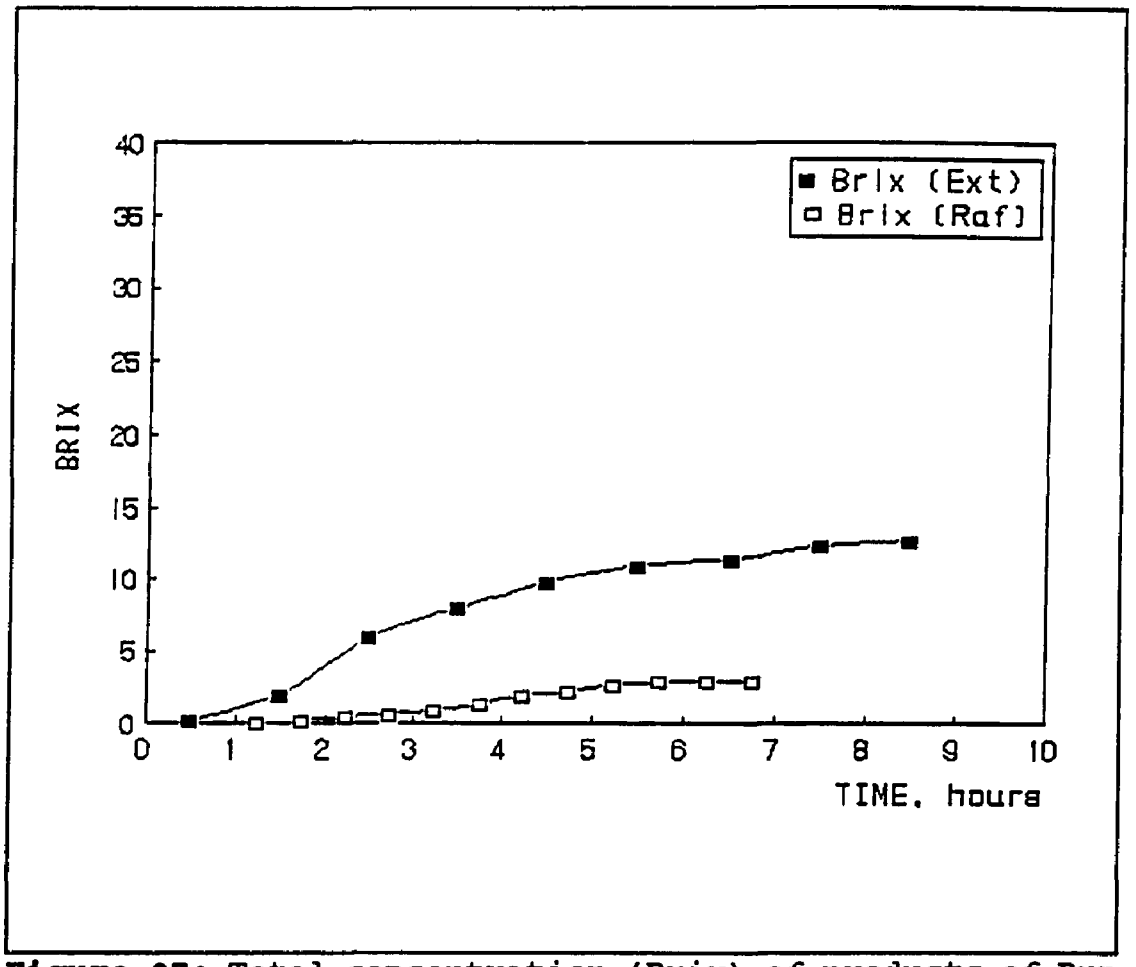

Figure 27: Total concentration (Brix) of products of Run #1.

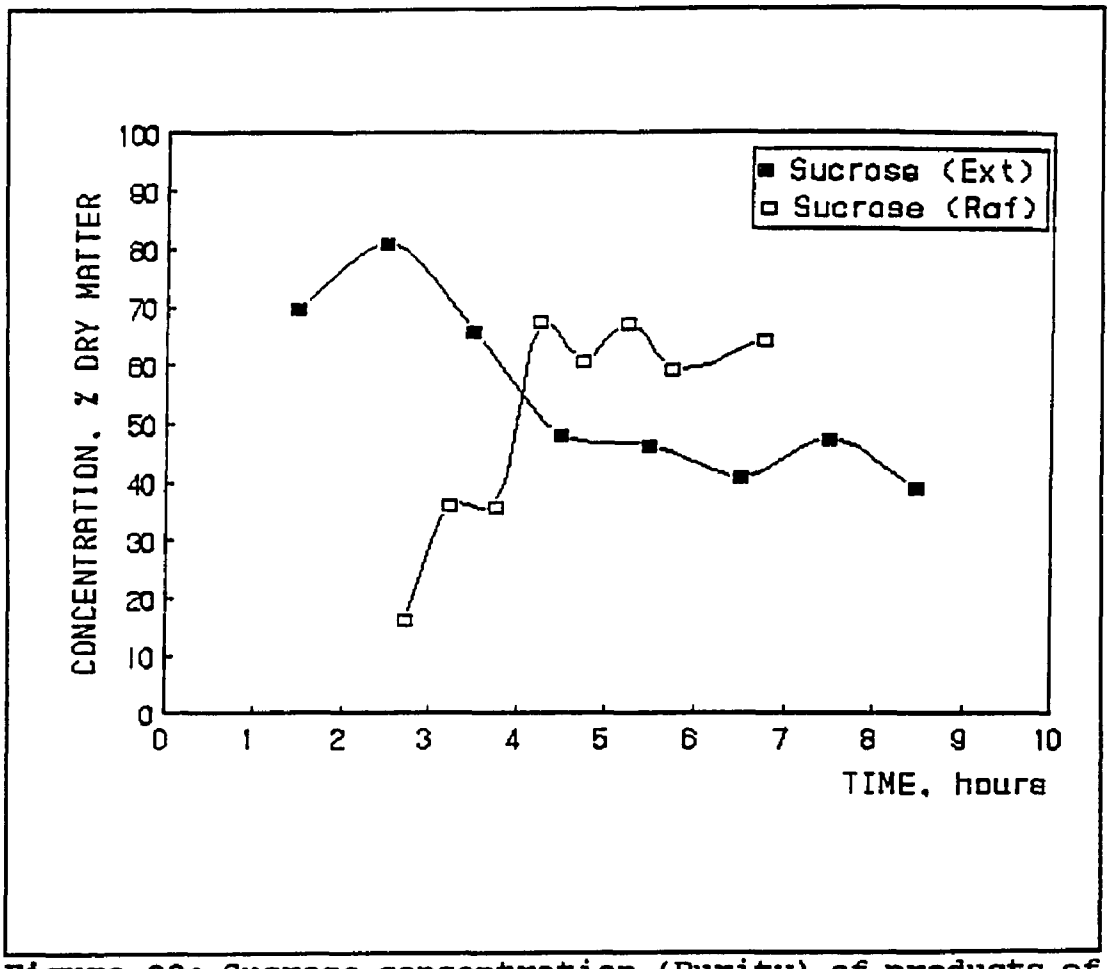

Figure 28: Sucrose concentration (Purity) of products of Run #1.

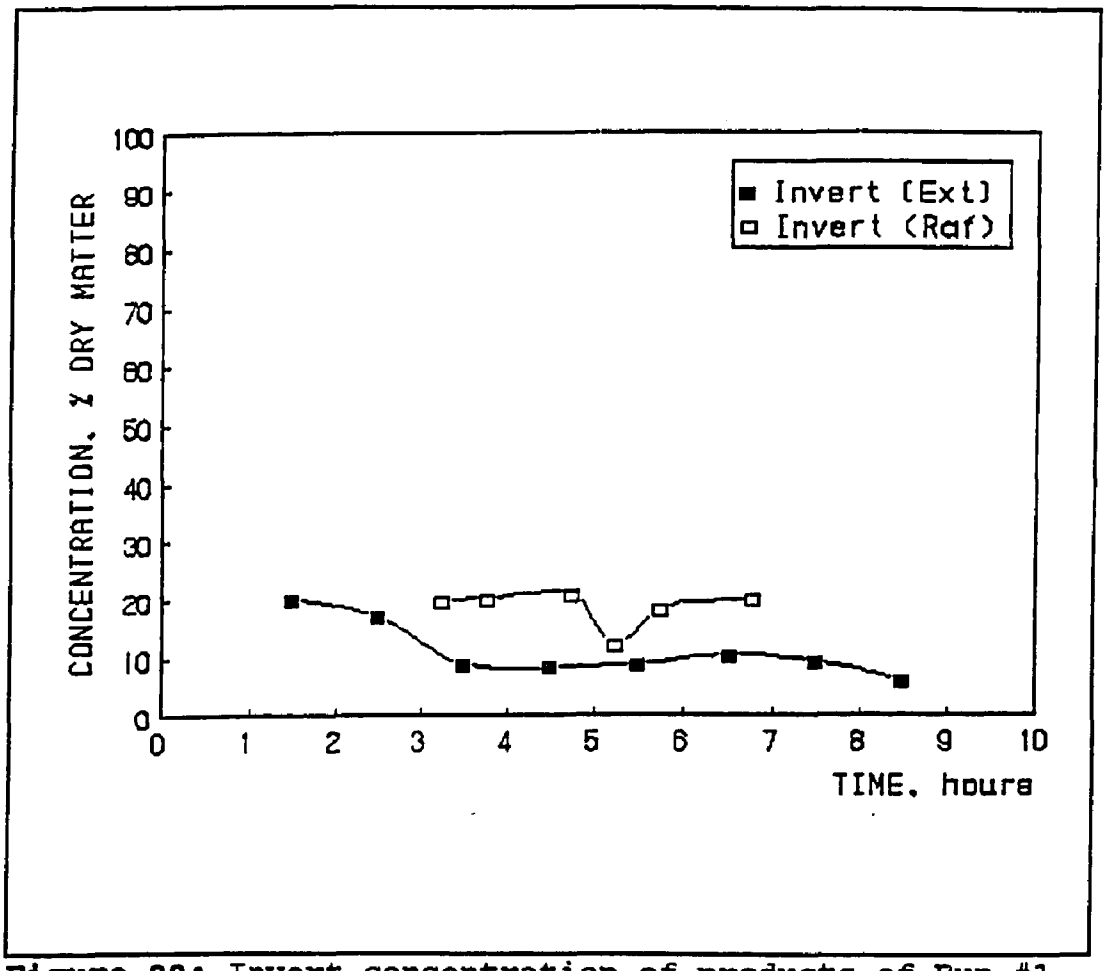

Figure 29: Invert concentration of products of Run #1.

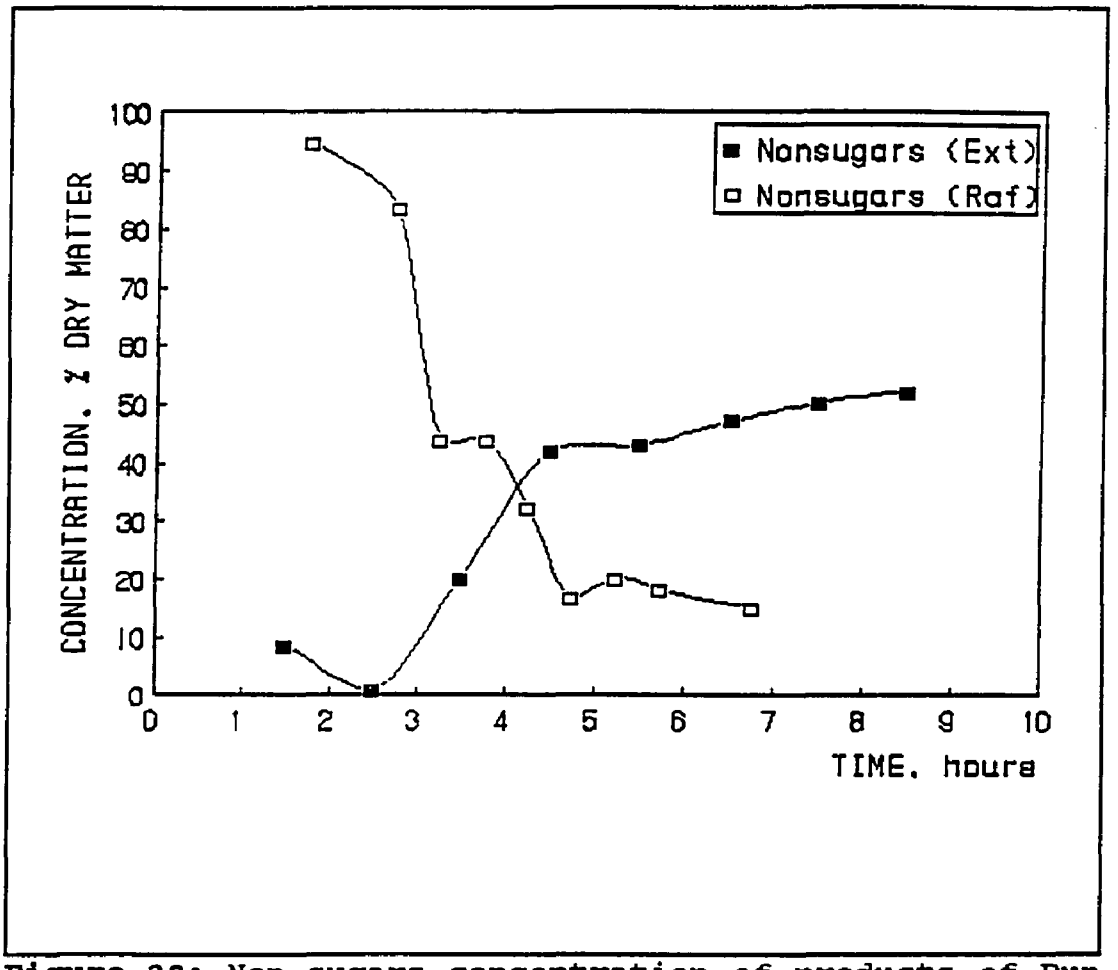

Figure 30: Non-sugars concentration of products of Run #1.

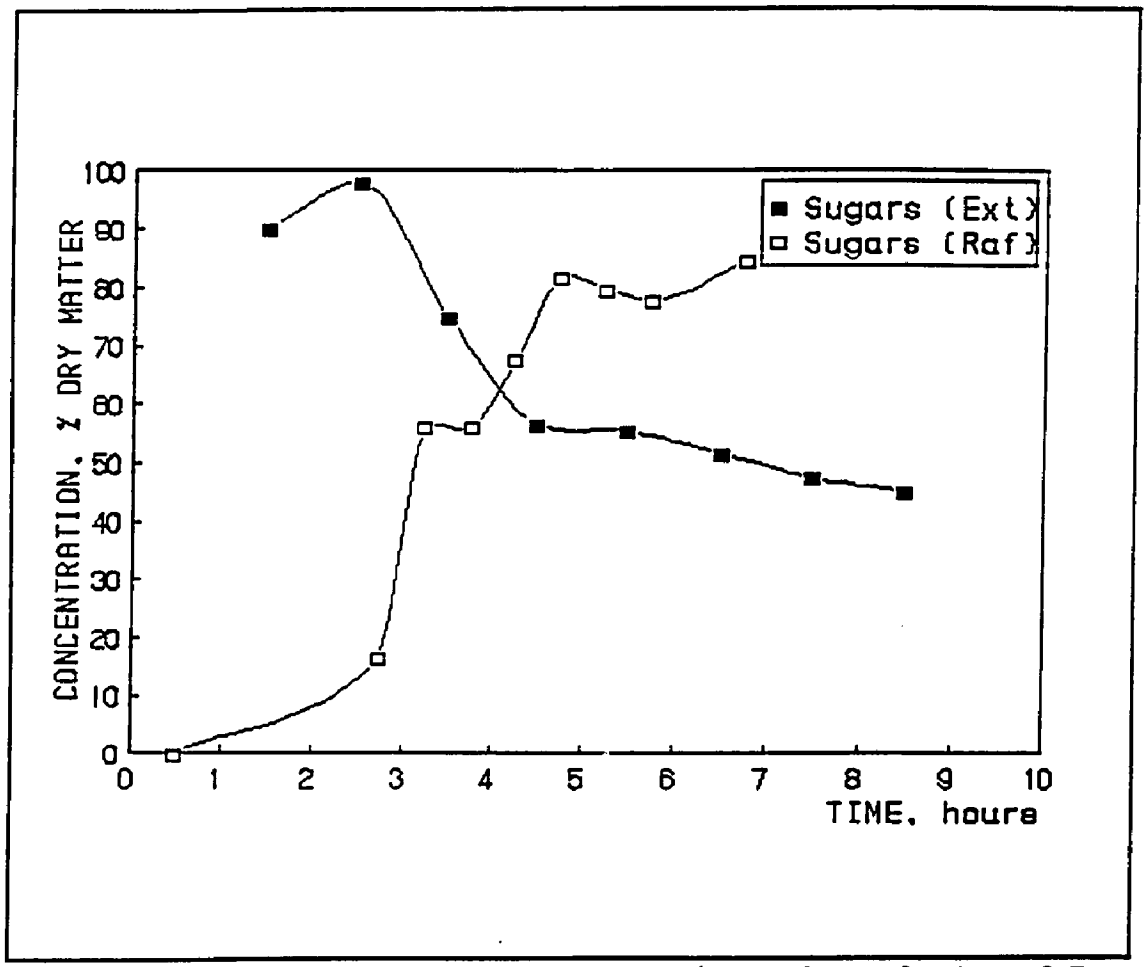

Figure 31: Total sugars concentration of products of Run #1.

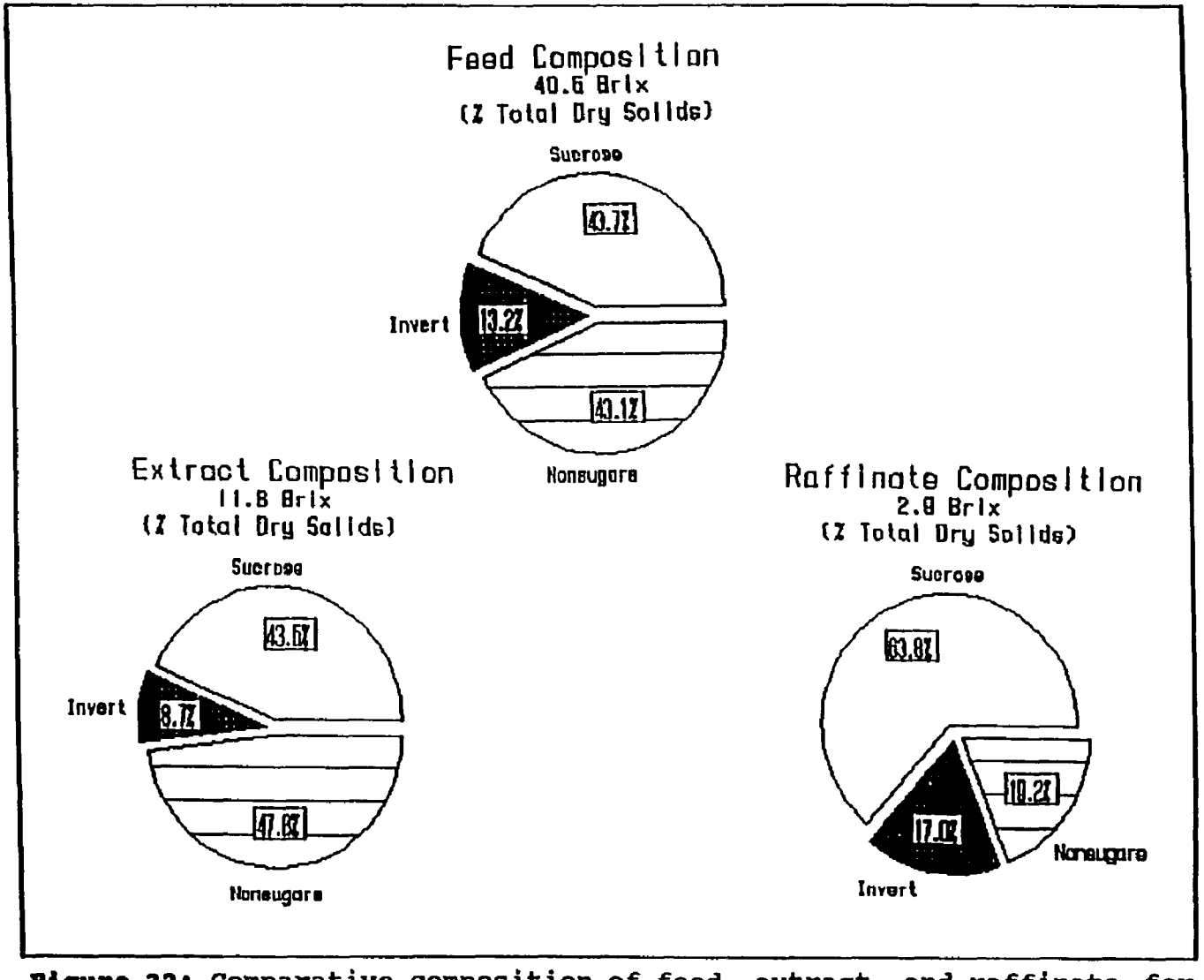

Figure 32: Comparative composition of feed, extract, and raffinate for Run #1.

Table 22:
Average composition of products Run #1 (on solids)

Product	Bx	Sucrose %	Invert %	Salts %	Sugars %	Color I.U.
Extract	11.8	43.5	8.7	47.8	52.2	35690
Raffin.	2.9	63.8	17.0	19.2	80.8	56075

It can be seen that the extract from Run #1 had almost the same composition as feed molasses (Fig 32). The raffinate had higher sugars but its concentration was so low that it was impractical to continue the experiment even with this "inverse separation". From separation point of view, the results of this experiment can be considered as insignificant.

Experiment Run #2

This experiment was started with the same parameters as for Run #1 (Table 8), but with better arrangement of sample analysis, the delay in getting the sample analyzed was reduced to about 15 minutes. It was possible because only extract samples were analyzed with the understanding that loss (if any) of separation can be observed by the dropping purity of the extract. The results are graphed and presented as Figs. 33 to 38.

After 3.8 hours, purity of the extract dropped much below 75 (Fig. 34). It was observed that purity of the fluid (in the upward column) was closer to extract purity. A longer switch time was tried to give more time to sugars

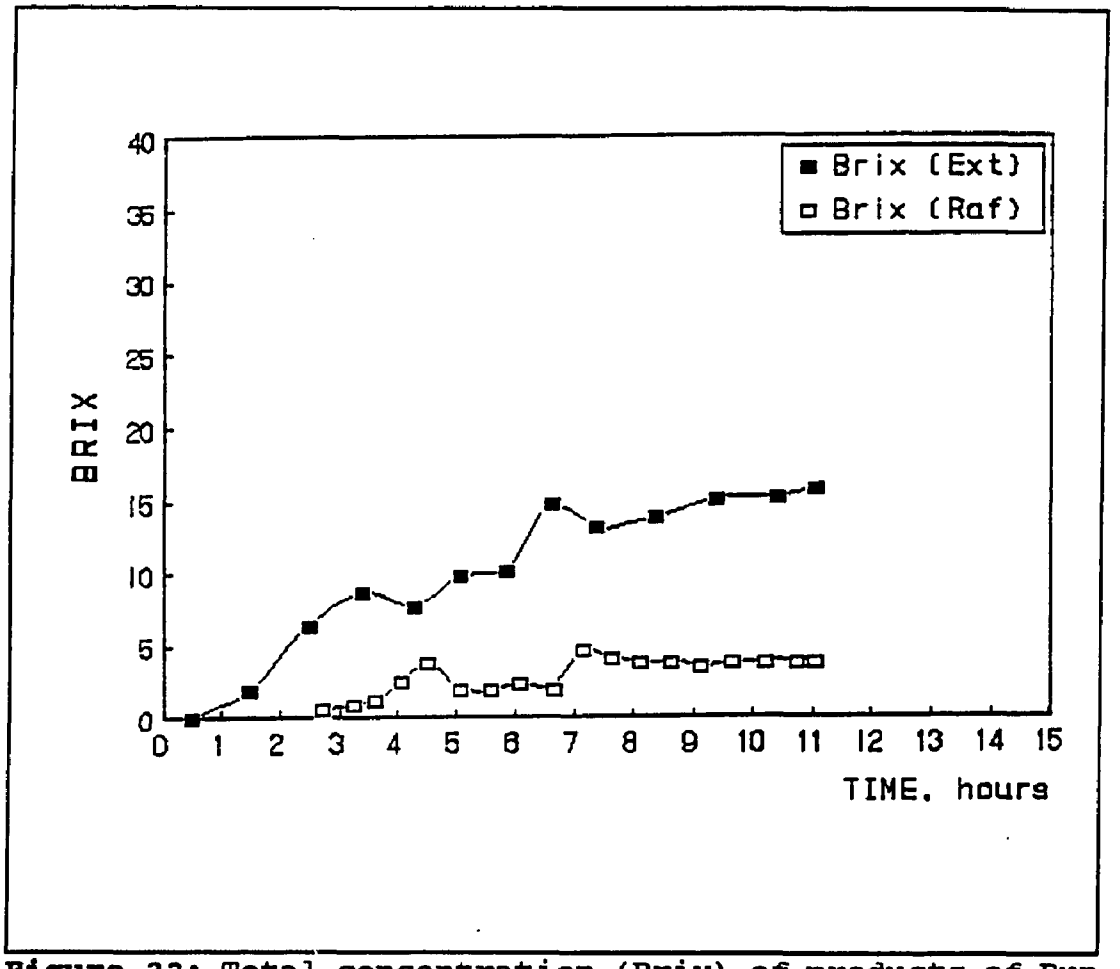

Figure 33: Total concentration (Brix) of products of Run #2.

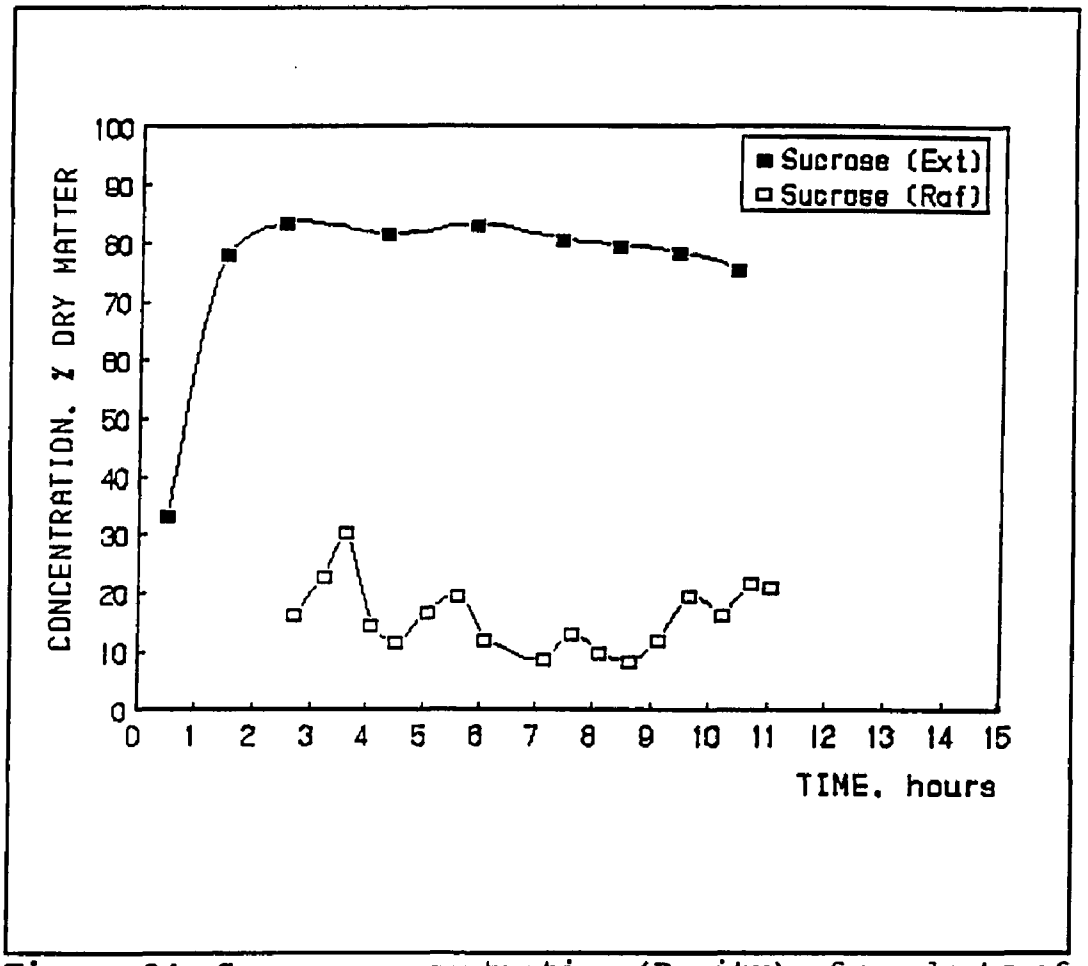

Figure 34: Sucrose concentration (Purity) of products of Run #2.

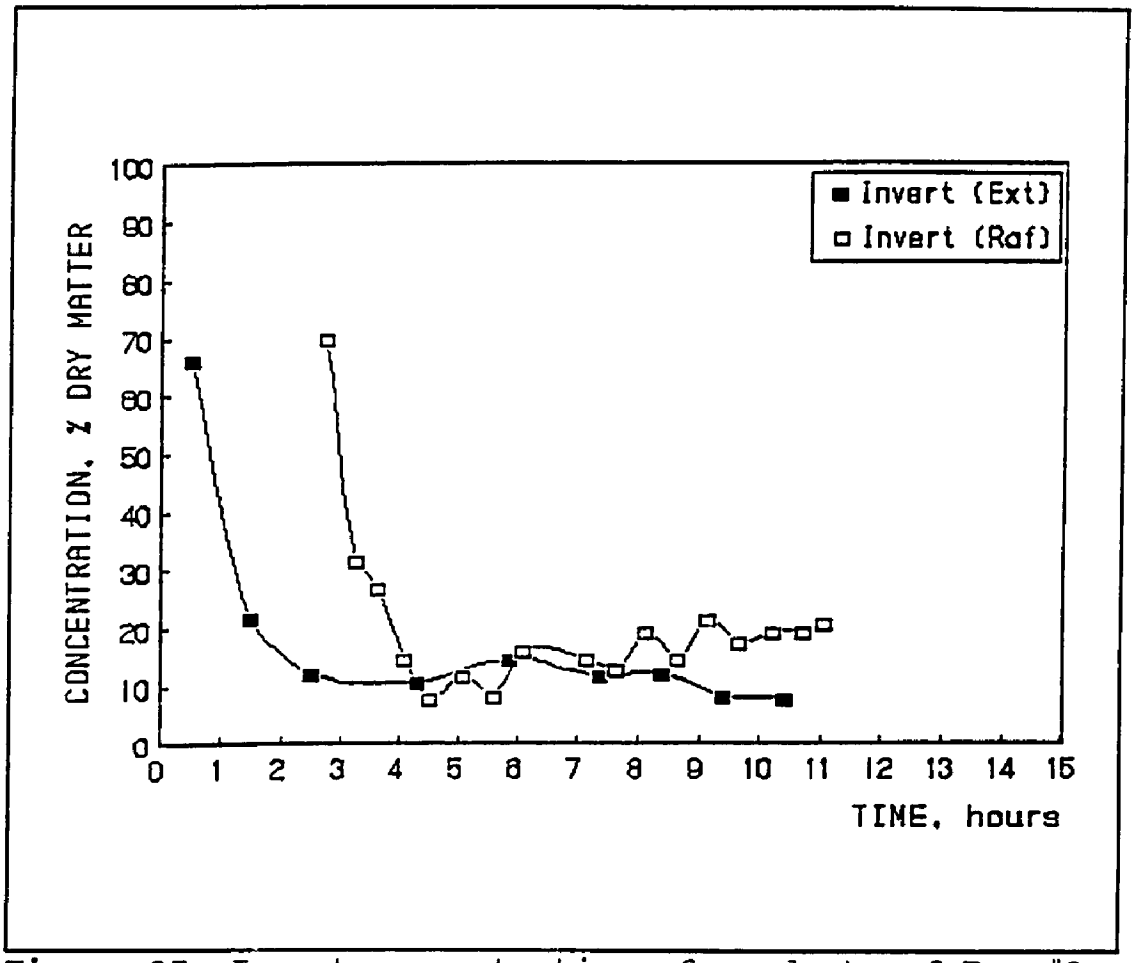

Figure 35: Invert concentration of products of Run #2.

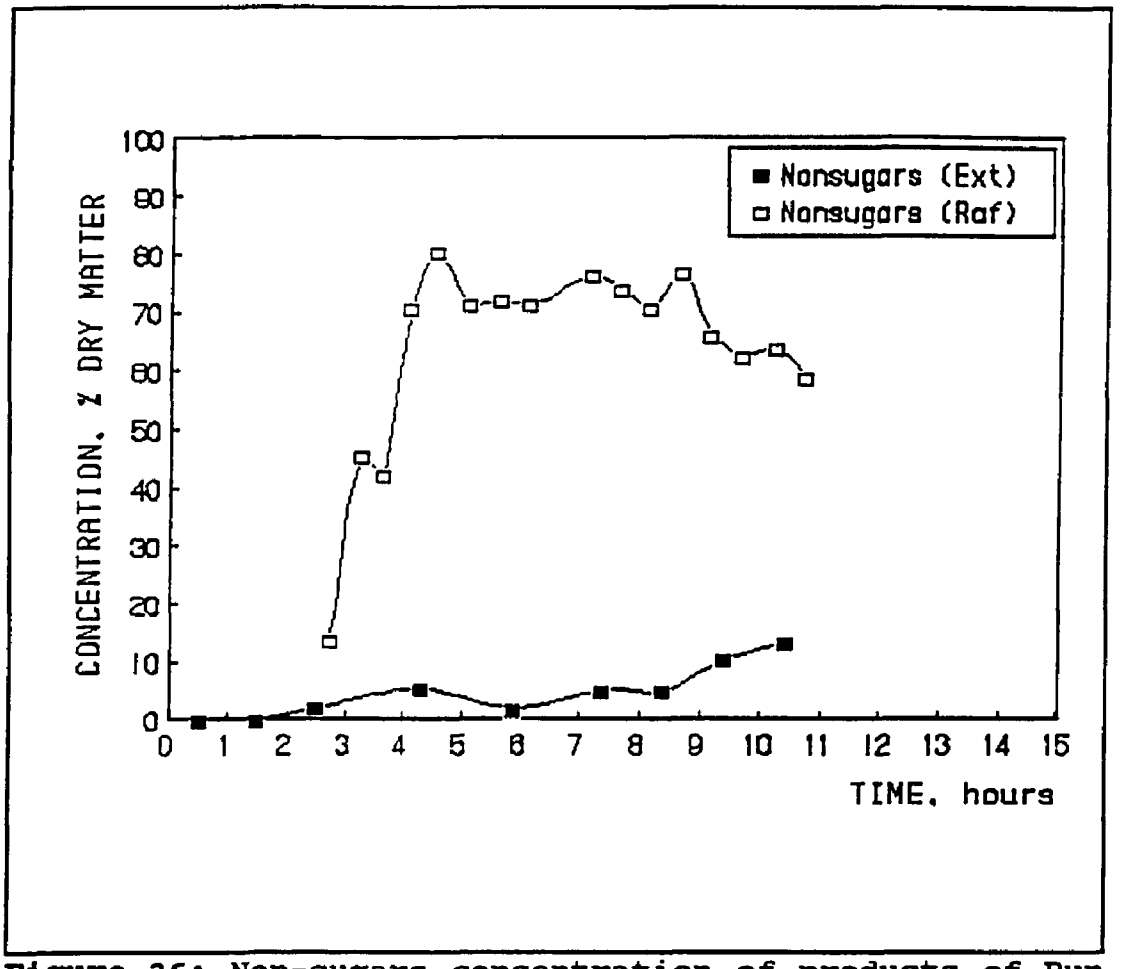

Figure 36: Non-sugars concentration of products of Run #2.

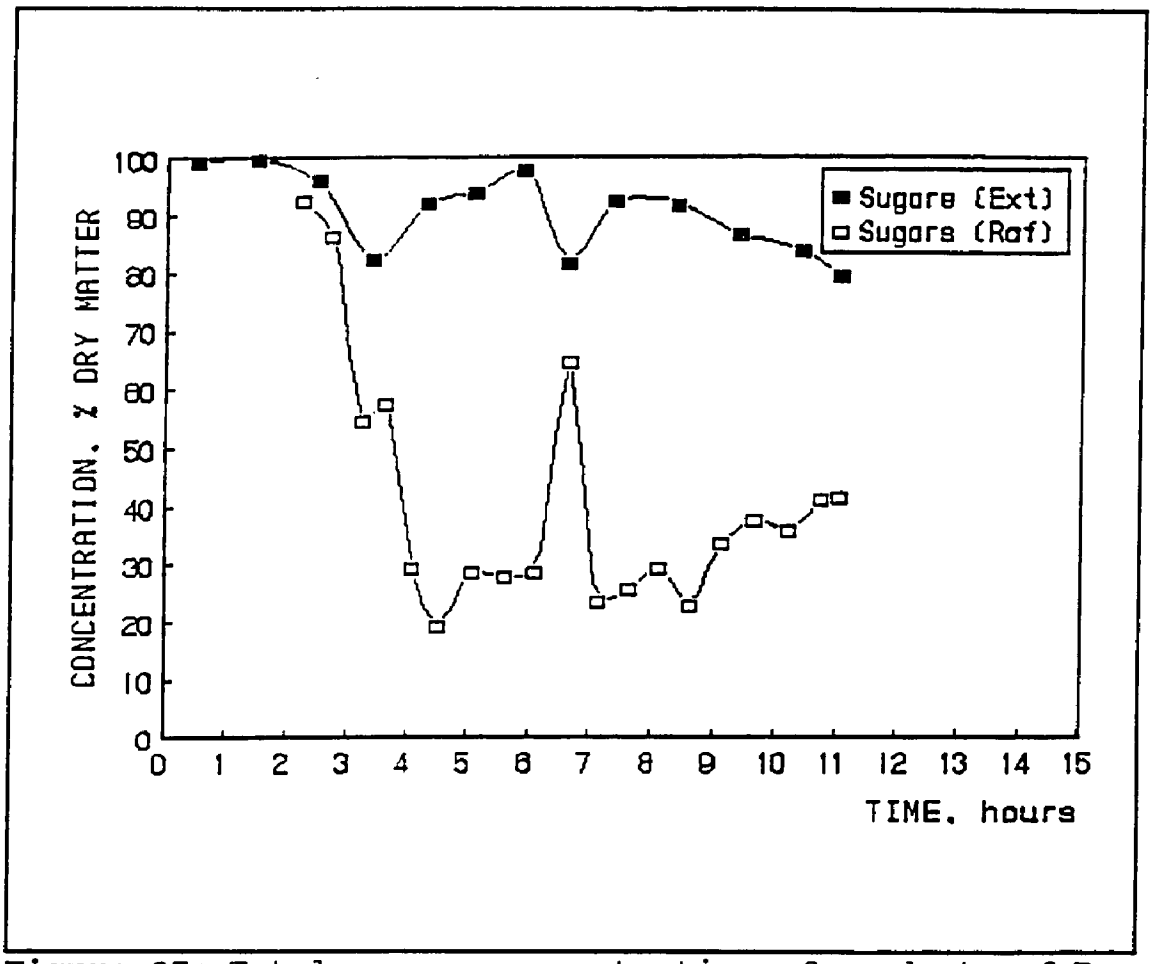

Figure 37: Total sugars concentration of products of Run #2.

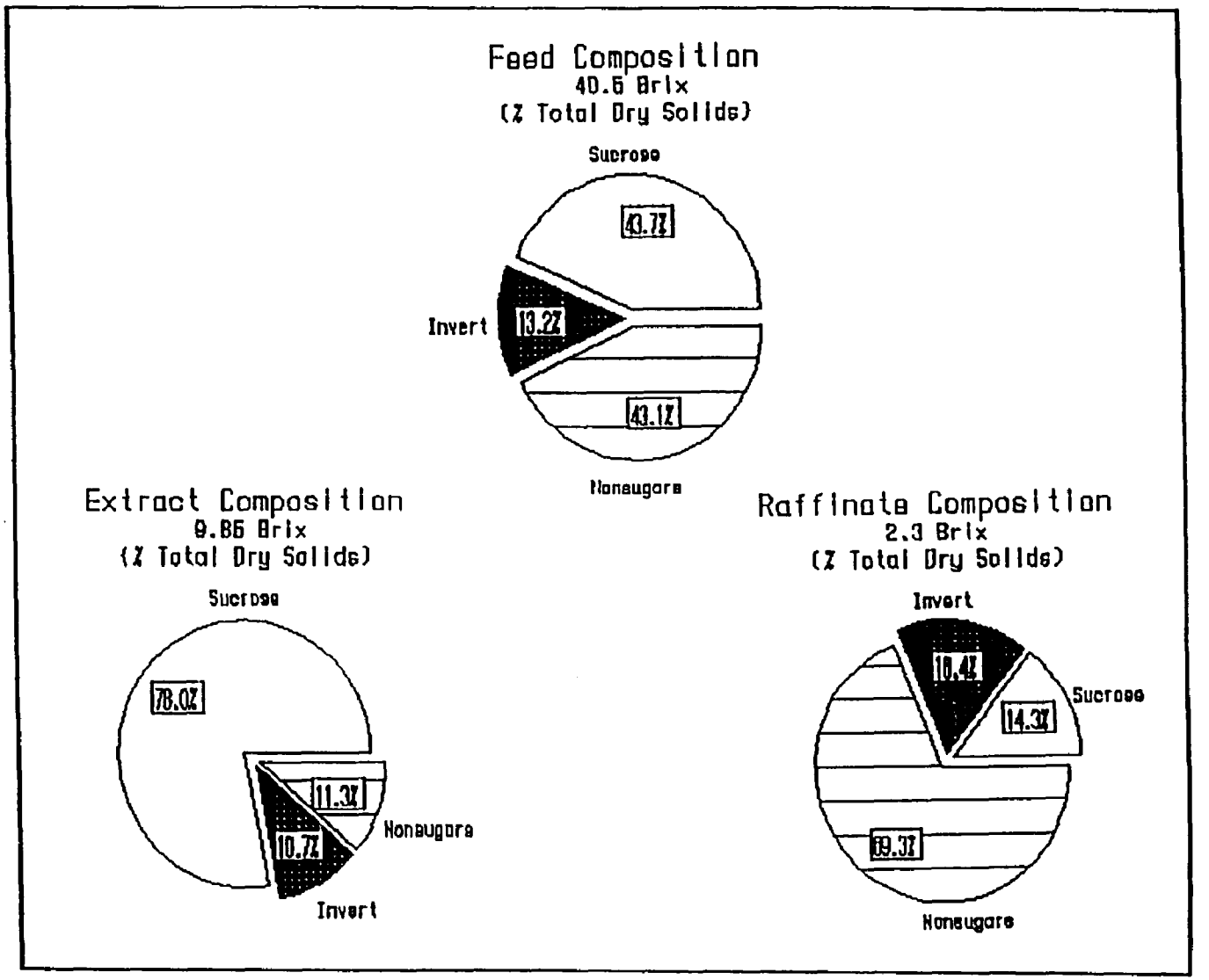

Figure 38: Comparative composition of feed, extract, and raffinate for Run #2.

to emerge at the appropriate exit, and not to accumulate onto the system. After 1.5 hours, switch time had to be shortened to 8.3 minutes to slow down the flow of sugars as the purity was observed higher in downward column instead of in expected one. The situation could not be improved, as purity again dropped below 75, thus switch time was set back to 8.6 minutes, and recycle flow rate was increased to 250 ml/min. The logic of increasing recycle flow was to increase the velocity of streams to bring the components to their respective exits. This corrective action worked and the experiment was continued for next 4.3 hours, till it was terminated. It is evident that purity of the extract was almost constant (Fig. 34) after corrective actions, but showed a decline in the end of the experiment. The same trend but in an opposite direction was observed for salts and invert in both the products (Figs. 35 & 36). The brix of the products (Fig. 33) gave no significant information about the pattern of the experiment. Brix seemed to be stabilized in the case of the raffinate with a downward trend in the end of the experiment. Whereas the extract brix showed a constant upward trend with some fluctuation in the beginning. The results shown in the said figures are of the products collected hourly (extract) and half hourly (raffinate) as it was realized that these samples are more representative under these conditions. Products for the period when the separation was upset, have not been included

in these figures. Average composition of the extract and raffinate is given in Table 23.

Table 23:
Average composition of products Run #2. (on solids)

Product	Brix	Sucrose %	Invert %	Salts %	Sugars %	Color I.U.
Extract	9.8	78.0	10.7	11.3	88.7	26577
Raffi.	2.3	14.3	16.4	69.3	30.7	119716

The purity of the extract is 78 and of raffinate is 14.3. It can be seen that the extract has a reasonable purity compared to that of feed molasses, where the total sugars in the extract was 88.7 %.

Recovery of sucrose in the extract was 87.1 %, invert was 43 %, and salts was 17 % (Tables 15 & 16). About 57 % of the invert had gone to the raffinate stream. It is clear that the raffinate still had a considerable amount of sugars (Table 23).

Concentration (total solids) of the extract was 24.3 %, and the raffinate 5.7 % of the feed molasses. These concentrations are very low from an industrial point of view. This could put an extra load on energy sources.

Color of the product extract was about one third that of feed molasses, whereas the raffinate color was much higher and reflected the "flow" of maximum colorant towards this stream as was expected.

It was observed that an increase in recycle flow rate helped to have an optimum separation between sugars and non-

sugars. It could be realized that a proper flow rate in the system is very essential for the separation desired. The last phase of the run showed a decline in the purity of the extract, which might have led to a poor separation if run would have continued. This means that some improvement in control of flow rates of the system is still needed.

Experiment Run #3

This experiment was run with a slow flow pattern within the system compared to Runs #1 and #2. A slower recycle flow rate was selected based on the findings that potassium chloride suppresses the separation of sucrose at higher flow rates (Saska et al., 1992). Recycle flow @ 50 ml/min along with a switch time of 18 minutes was tried as starting conditions, Table 8. The results of this run are graphed as in Figs. 39 to 44. After 4.23 hours, approximate time for the system to reach the steady state, a continuous drop in the extract purity was observed (Fig 40). Recycle flow rate was increased realizing that overall flow within the system was low and caused low purity of the extract, since sugars were not being pushed towards the appropriate exit. After 7.85 hours, recycle flow rate was further increased for the same reason. The run had to be terminated as no improvement in the situation was expected. Purity of the extract kept dropping after the system reached a steady state, and it could not be improved in spite of corrective actions.

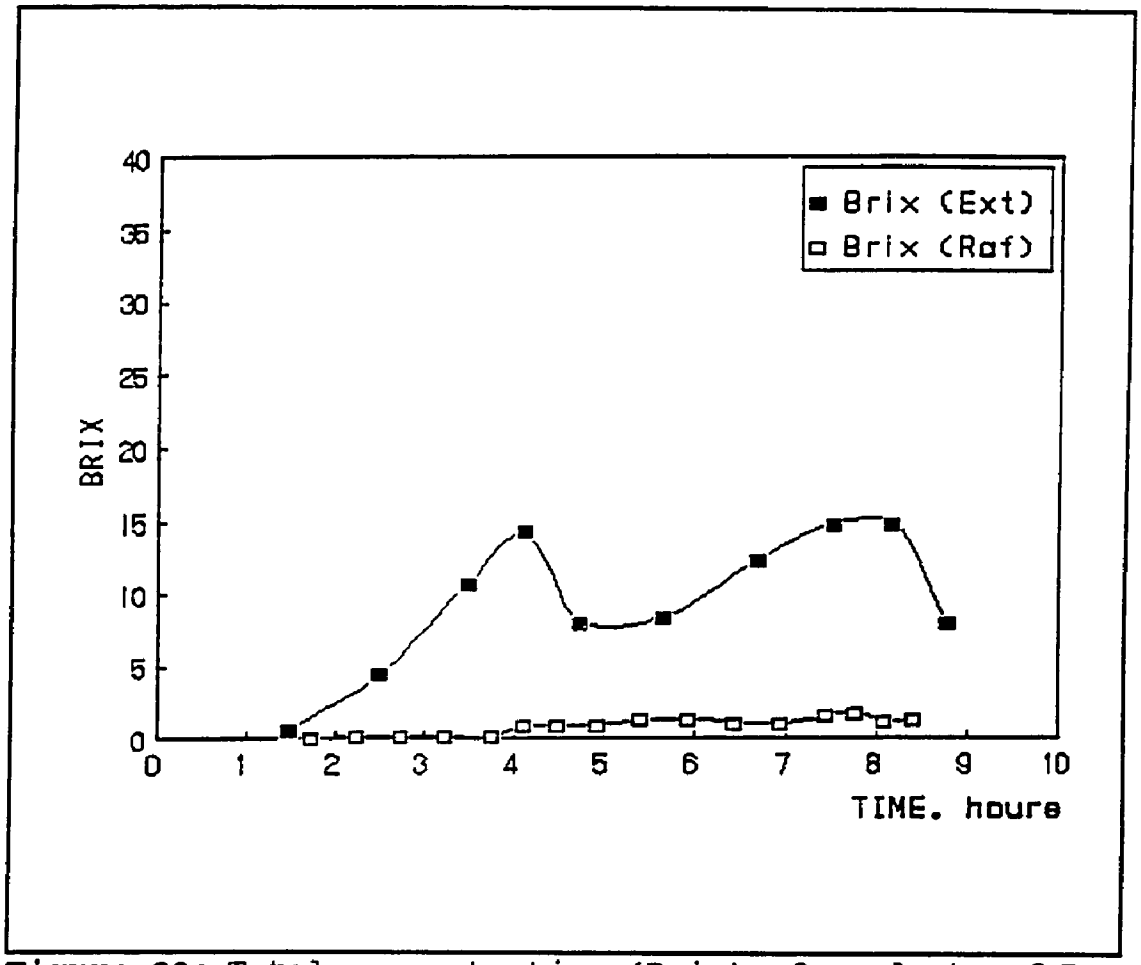

Figure 39: Total concentration (Brix) of products of Run #3.

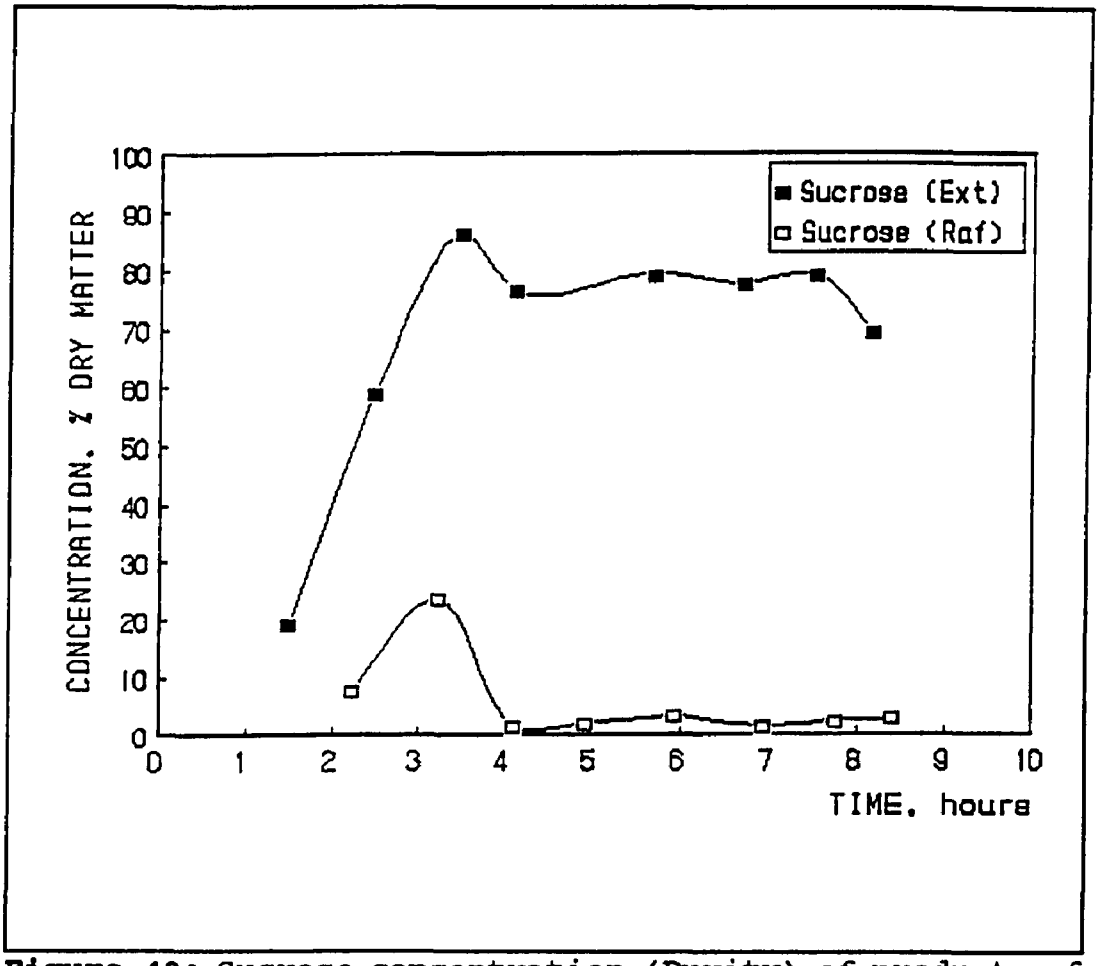

Figure 40: Sucrose concentration (Purity) of products of Run #3.

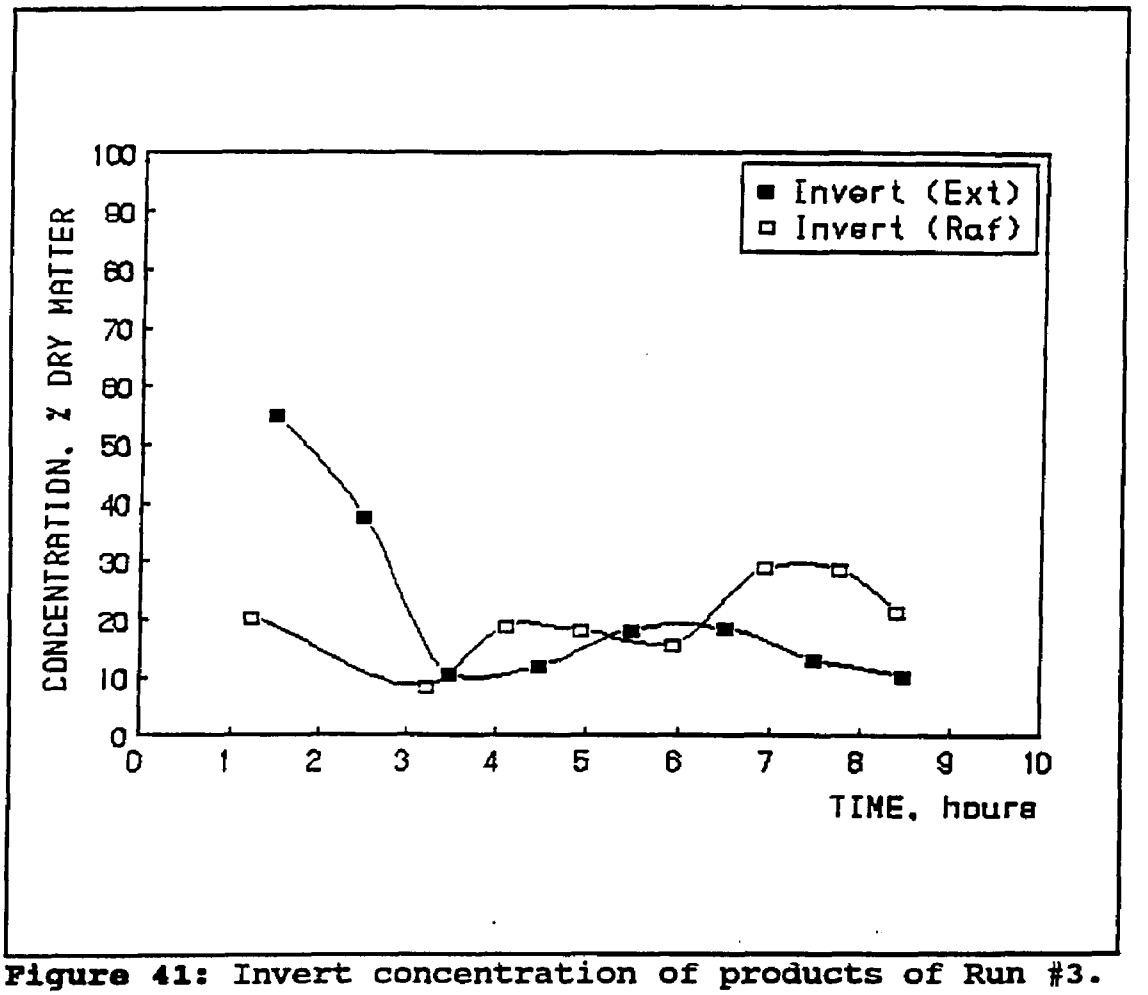

Figure 41: Invert concentration of products of Run #3.

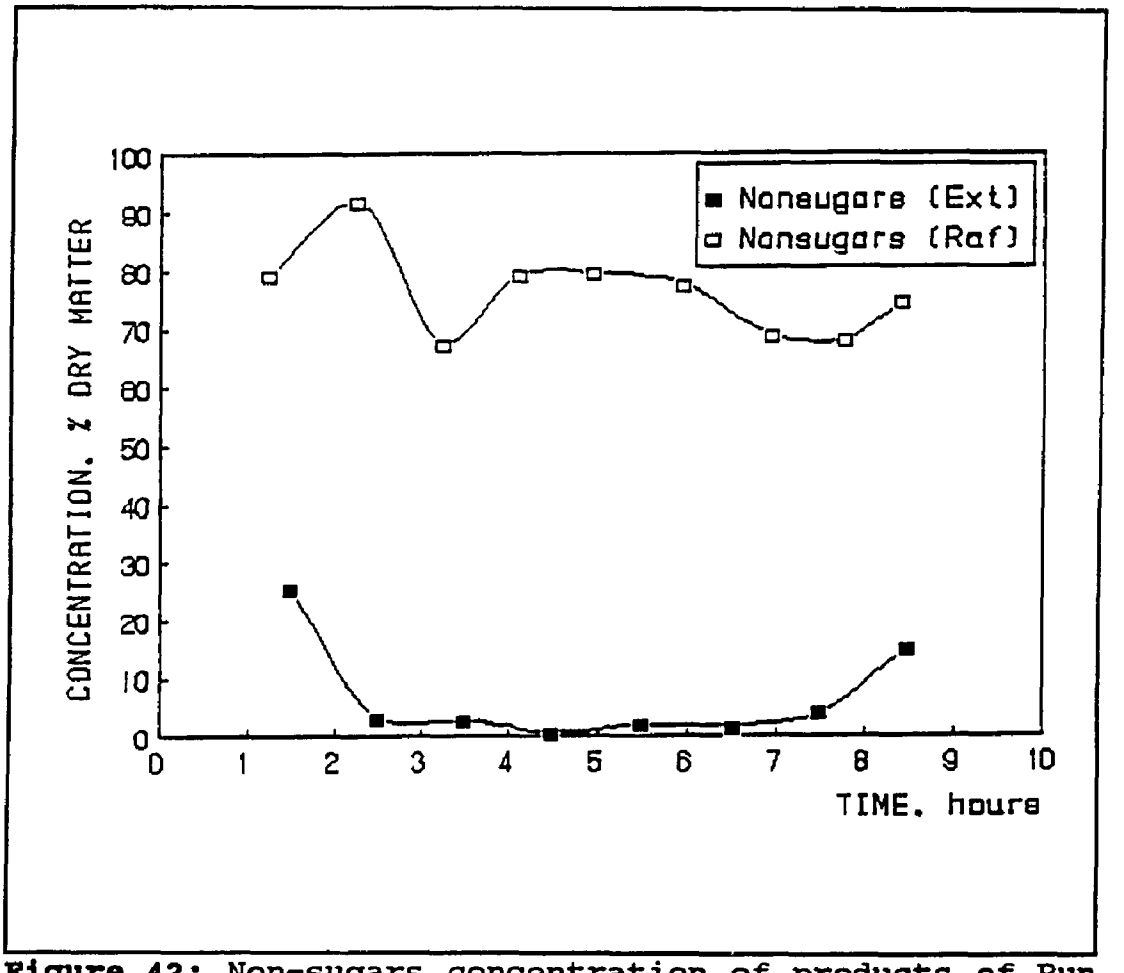

Figure 42: Non-sugars concentration of products of Run #3.

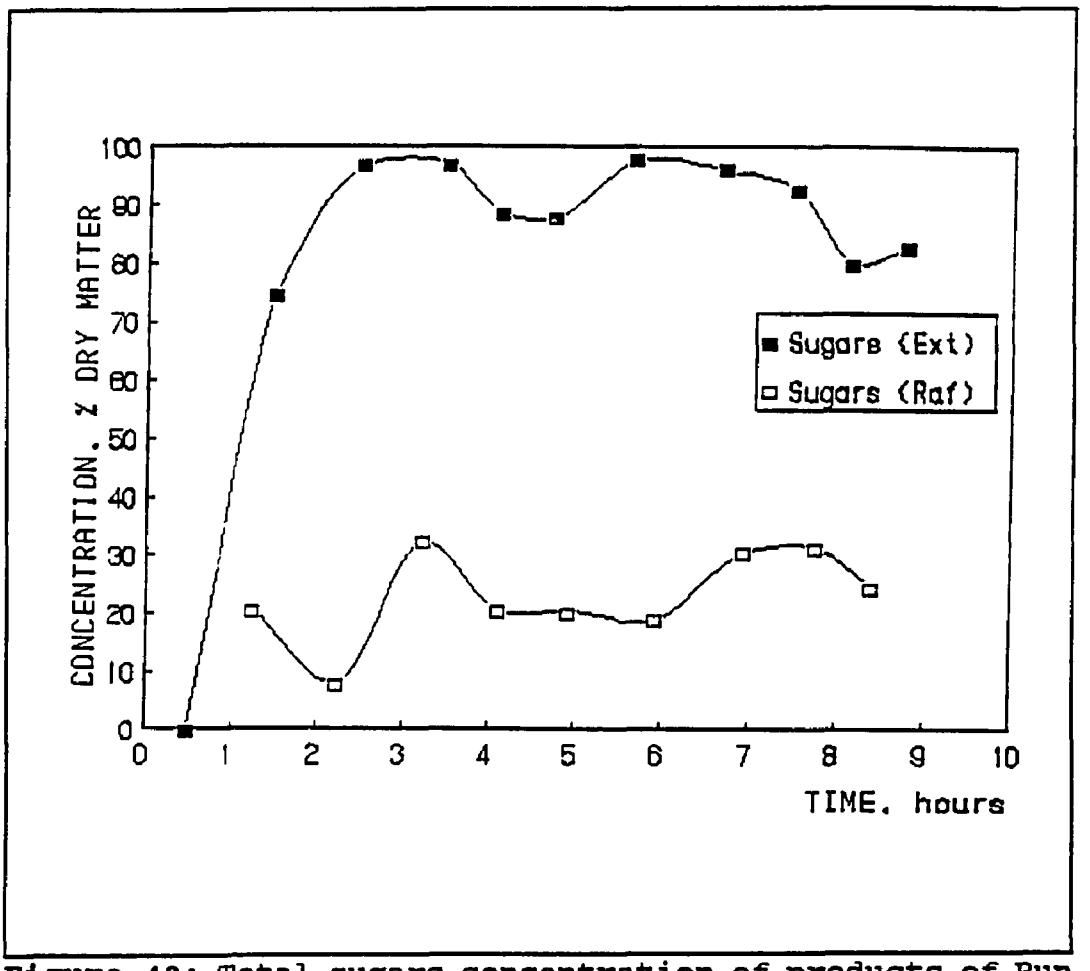

Figure 43: Total sugars concentration of products of Run #3.

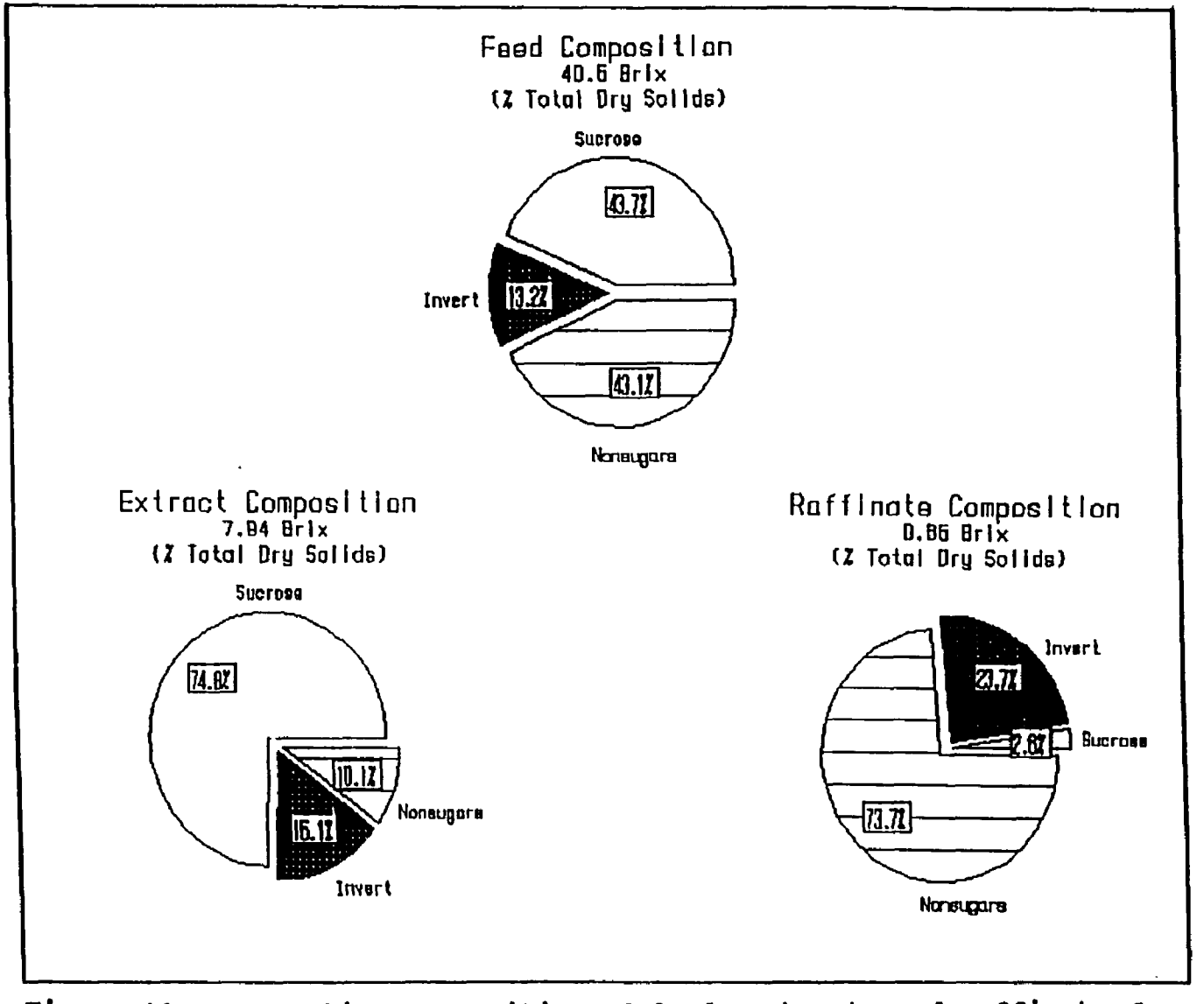

Figure 44: Comparative composition of feed, extract, and raffinate for Run #3.

Average composition of the extract and the raffinate is given in Table 24.

Table 24:
Average composition of products Run #3 (on solids).

Product	Brix	Sucrose %	Invert %	Salts %	Sugars %	Color I.U.
Extract	7.9	75.4	15.7	8.9	91.1	17802
Raffi.	0.8	3.4	19.9	76.6	23.4	154868

The average purity of the extract is 75.4 and of raffinate is 3.4. The purity of the extract is just close to our target set for running the experiment.

Recovery of sucrose in the extract is 98.5 %, invert is 69.6 %, and salts is 25.3 %. In this run about 30 % invert is in the raffinate.

Concentration of the extract is 19.5 %, and the raffinate is 1.95 % of the feed molasses. These concentration are very low, specially of the raffinate.

Color of the extract is about one fourth of the feed. Whereas, the color of the raffinate is much higher compared to the feed.

It was observed that such a slow flow pattern within the system does not work. Though a slow flow helps to reach the equilibrium earlier, but in the SMB system, with a slow flow, a longer switch time is required to meet the other requirements such as column loading. Feed introduced in the longer switch time acquires more volume of the resin, thus mass transfer zone is reduced, which eventually affects the

separation. At the same time, introduction of water for a longer period causes unnecessary dilution of the products.

The assumption that potassium chlorid suppress the separation of sugars at higher flow rates does not prove to be correct in the case of molasses desugarizing by the SMB system. It can be assumed that the findings were based on pure potassium chloride and sucrose (in a binary solution) interaction during pulse testing. Whereas, in case of molasses, the interaction between potassium chloride and sucrose was suppressed or negated by the presence of other salts and sugars such as glucose and fructose.

Experiment Run #4

This experiment was started with the same parameters as of Run #2 with a slight increase in recycle flow rate (Table 8). The results of this run are presented in Figs. 45 to 5o. The rise in the extract purity was as expected till the system reached the steady state in about 5 hours (Fig. 46). The purity was constant till 8.5 hours, when it dropped. Based on the experience gained, recycle flow rate was increased to 265 ml/min, as a corrective action. After about 11.3 hours, the recycle flow rate was increased to 280 ml/min for the same problem. After this adjustment, the experiment continued for the next 14 hours, till all the available feed was consumed. In the last 5 hours of the

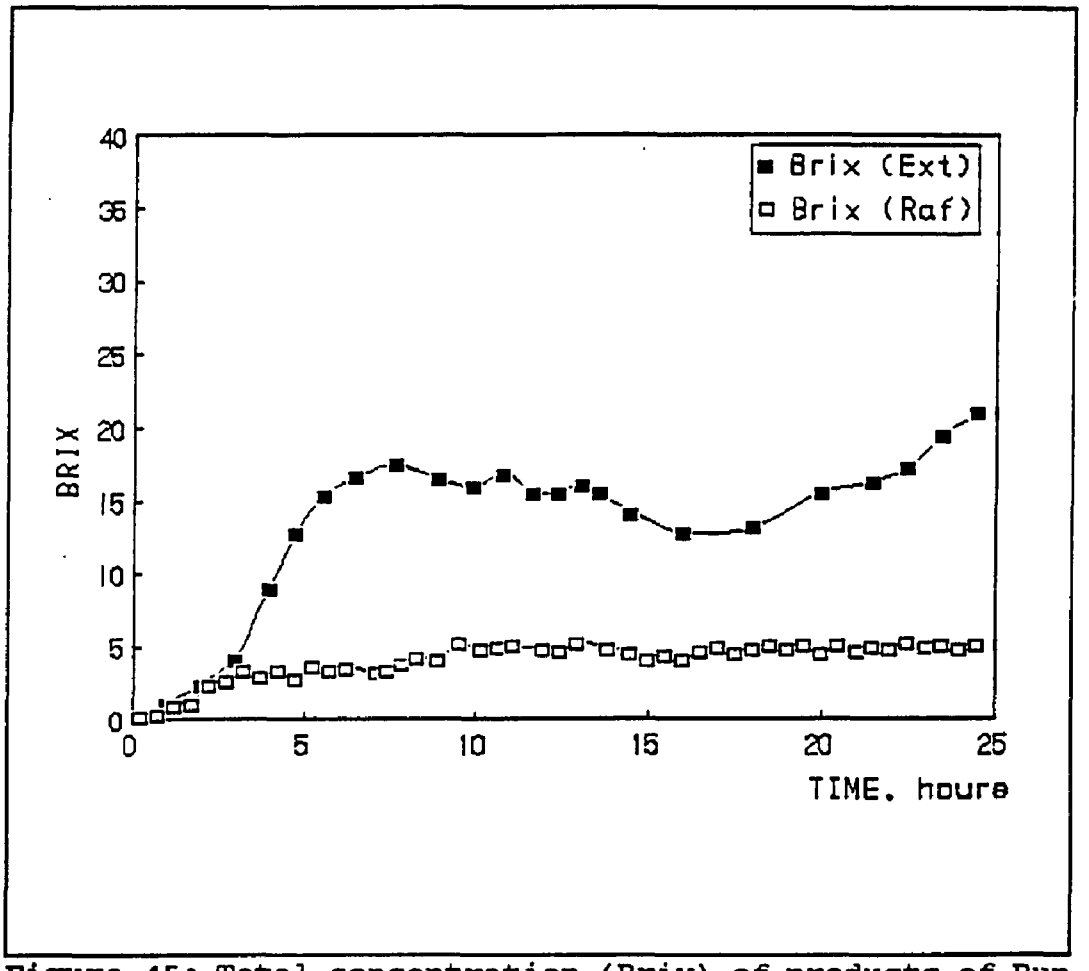

Figure 45: Total concentration (Brix) of products of Run #4.

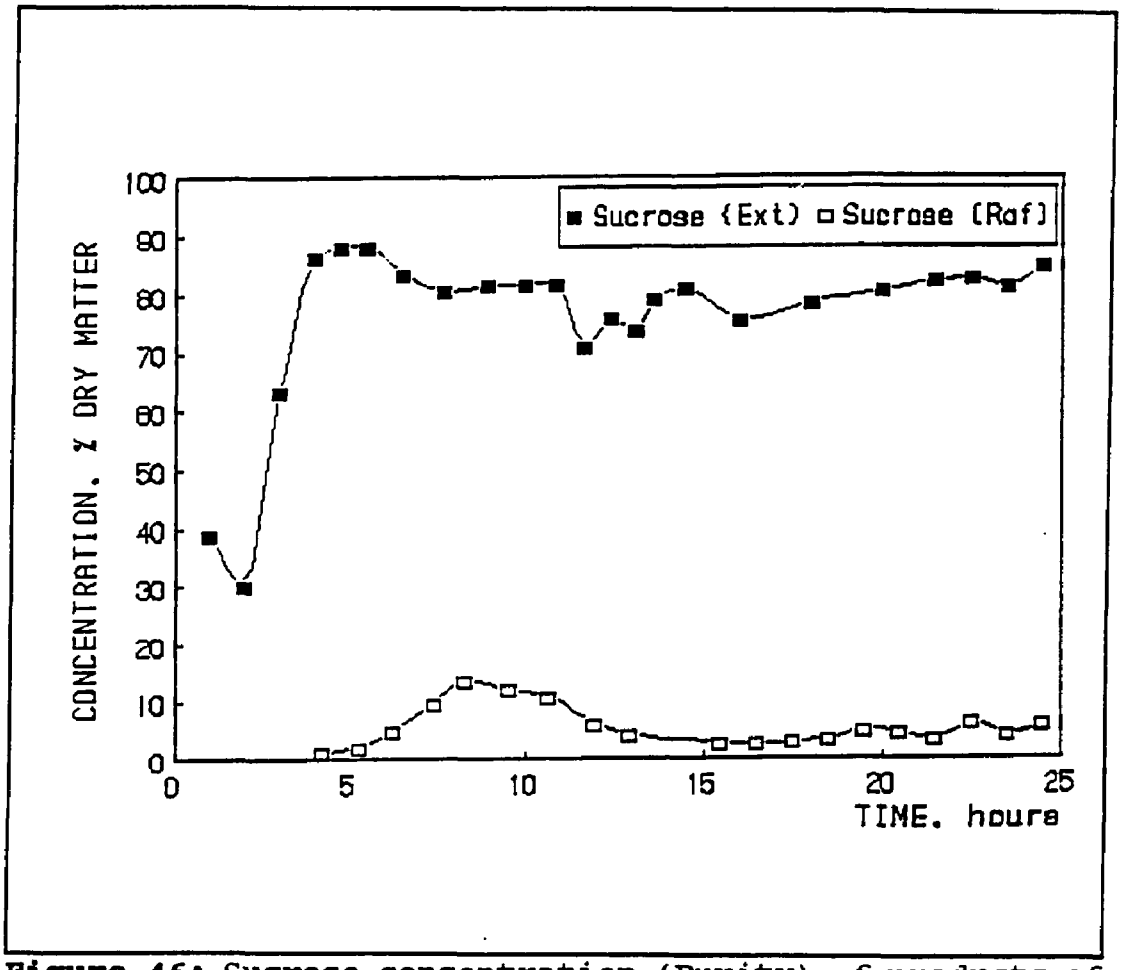

Figure 46: Sucrose concentration (Purity) of products of Run #4.

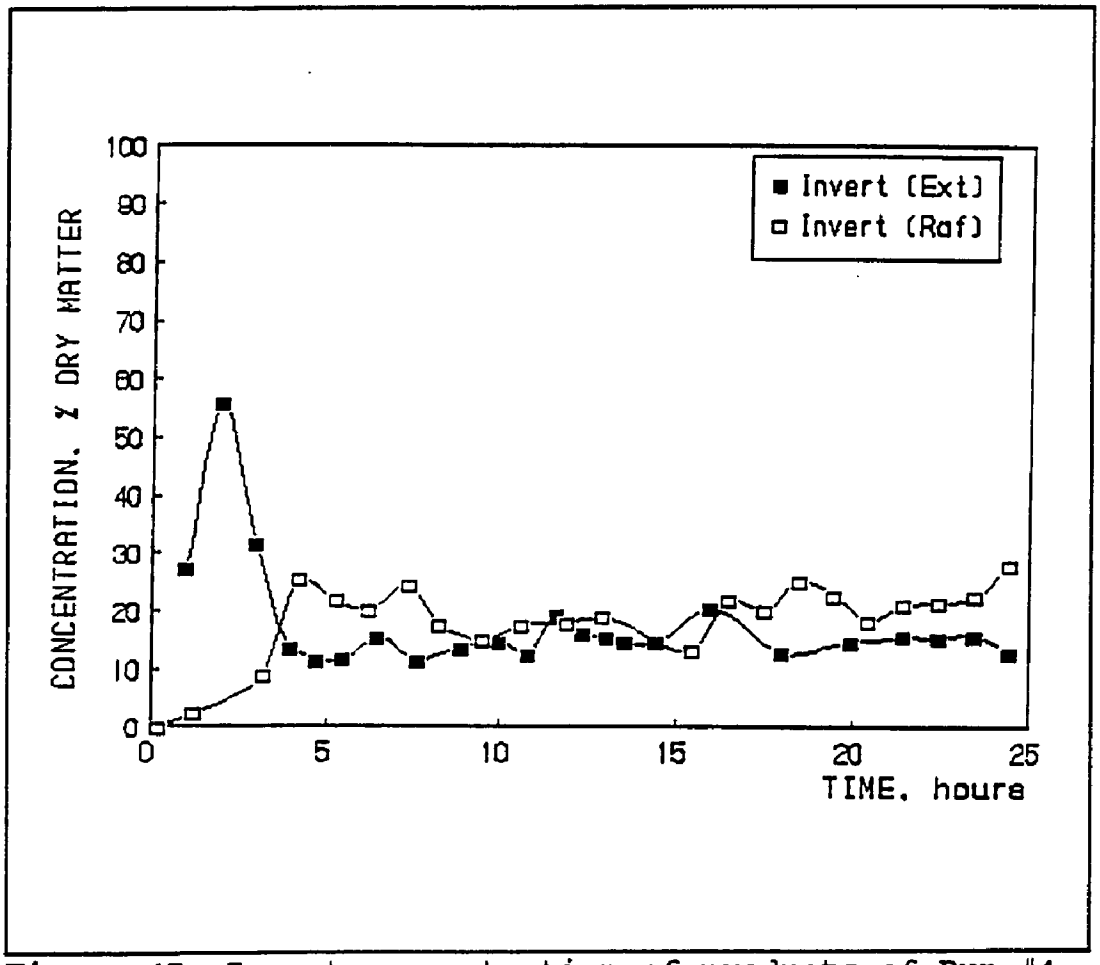

Figure 47: Invert concentration of products of Run #4.

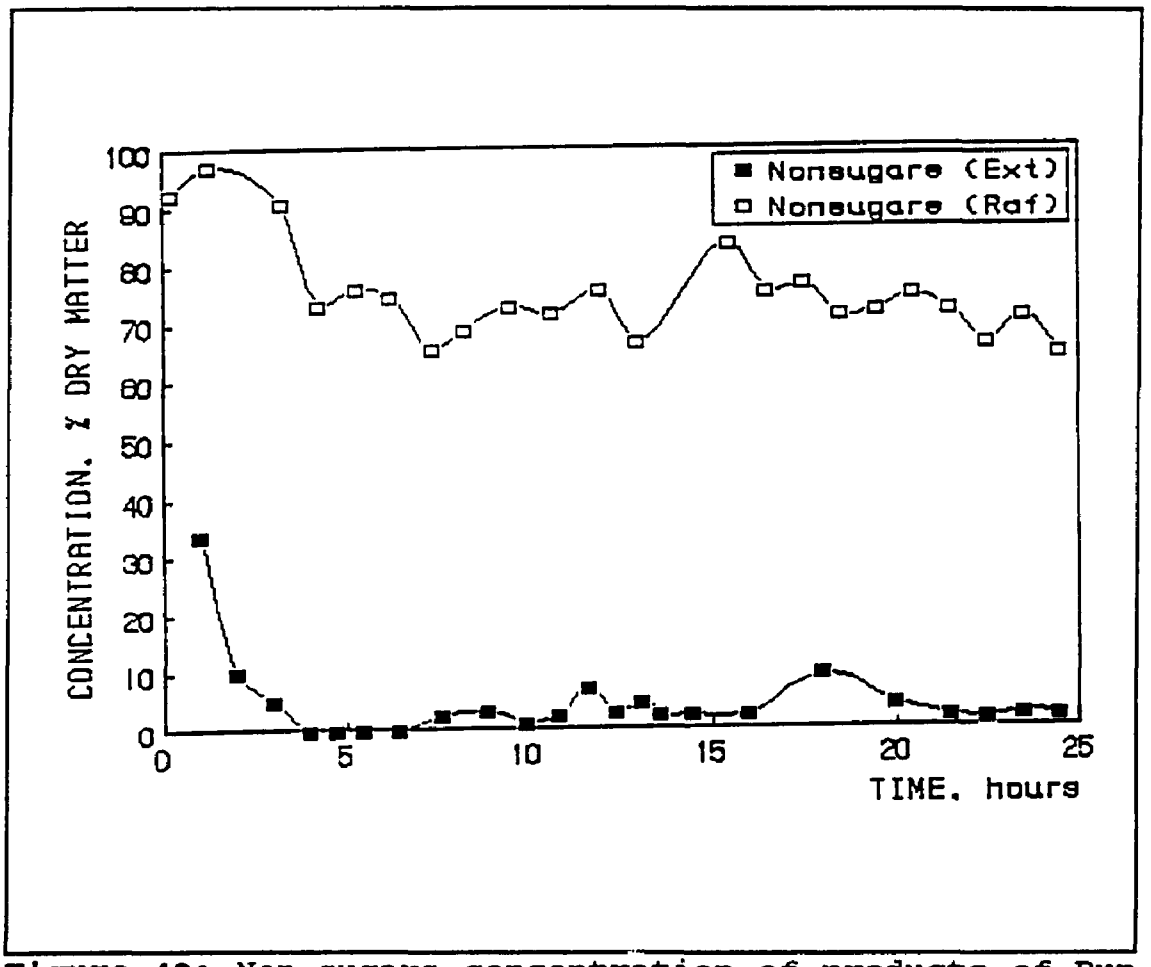

Figure 48: Non-sugars concentration of products of Run #4.

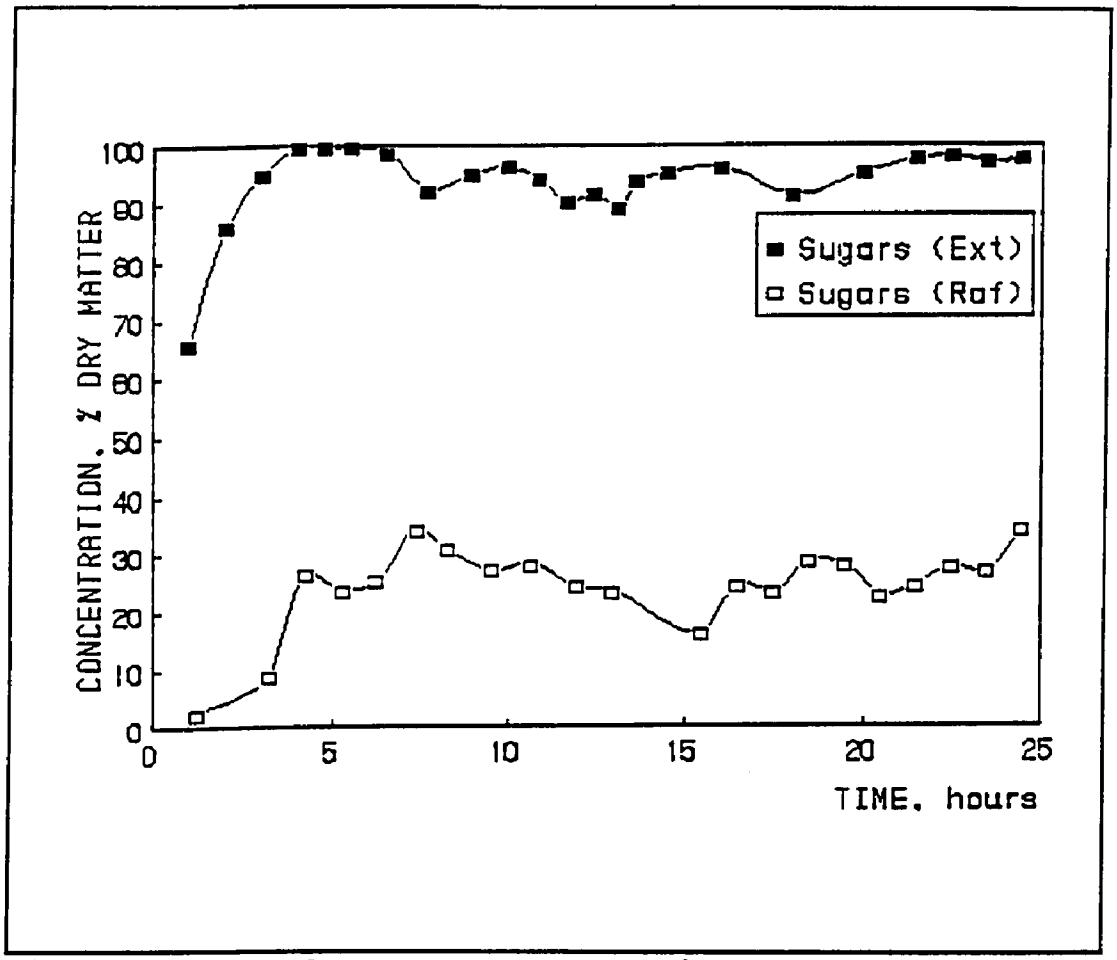

Figure 49: Total sugars concentration of products of Run #4.

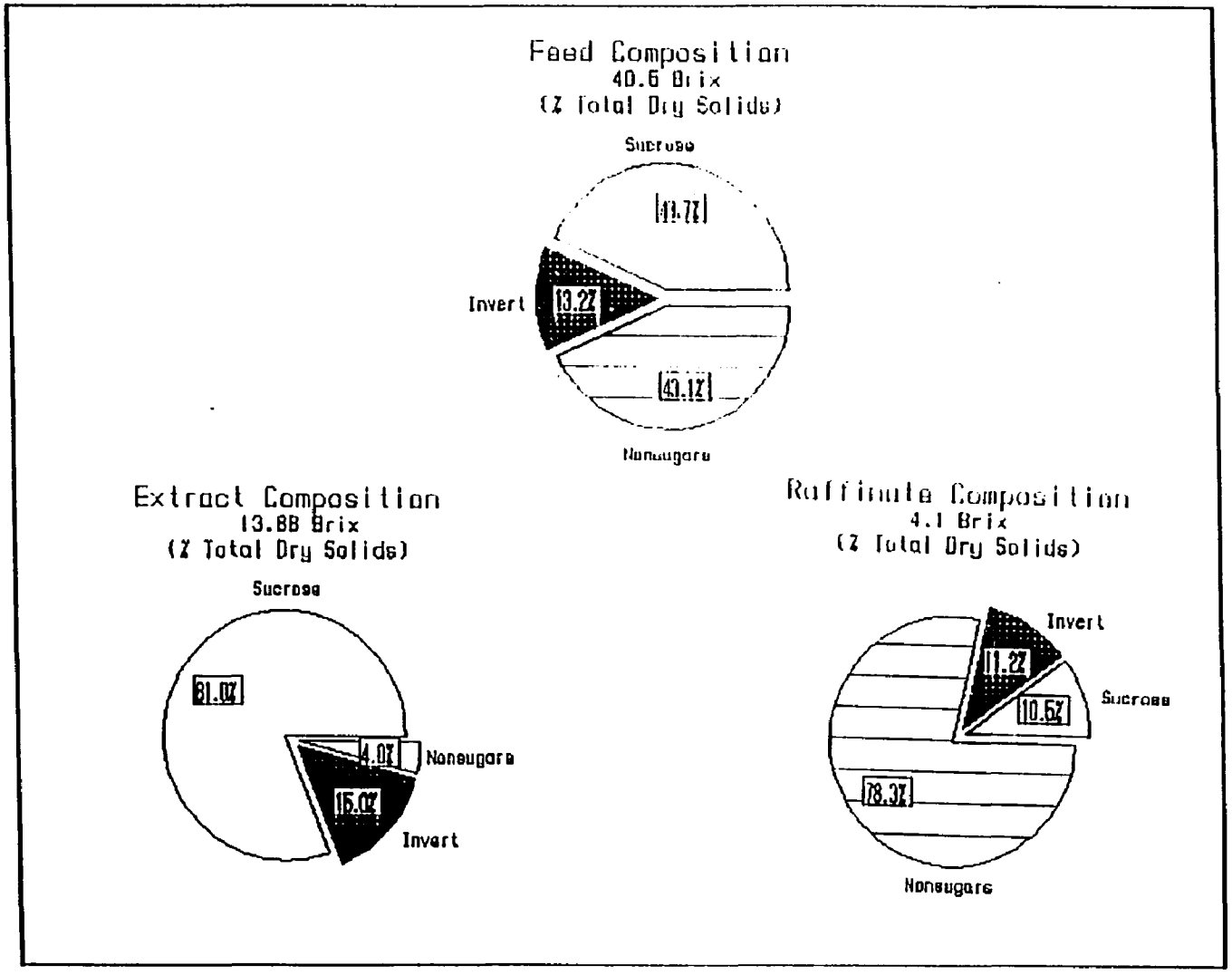

Figure 50: Comparative composition of feed, extract, and raffinate for Run #4.

experiment, the feed concentration was higher (i.e. 48.0 Brix), than the concentration at the start of the experiment due to overheating of feed molasses. But this had a positive effect on the purity as well as the brix of the extract. A continuous upward trend of the purity can be seen in the latter part of the run (Fig. 46). This is also true for the concentration of the extract (Fig. 45), it continued rising in the latter part of the experiment.

Average composition of the extract and the raffinate is given in Table 25.

Table 25:
Average composition of products Run #4 (on solids).

Products	Brix	Sucrose %	Invert %	Salts %	Sugars %	Color I.U.
Extract	13.9	81.0	15.0	4.0	96.0	16900
Raffi.	4.1	10.5	11.2	78.3	21.7	82300

The average purity of the extract was 81.0 and of raffinate, 10.5. This purity is higher than found in previous runs. Whereas, the percentage of total sugars for the extract was 96 and for the raffinate, 21.7, which is also higher than the previous runs.

Recovery of sucrose in the extract is 86.5 %, invert is 52.5 %, and salts is 4.1 %. Total sugars recovery is 78.5 %. In this run about 48 % invert has is in the raffinate. This made the total sugars in the raffinate to about 22 %.

Concentration of solids of the extract is 33 % , and the raffinate is 9.5 % of the feed molasses concentration.

Though these values are not still appropriate from industrial point of view, but are better than what was for previous runs.

Color of the extract is about one fourth of the feed. The color of the raffinate is slightly higher than the feed. This is similar to the previous runs. It can be assumed that mere color of the products is not a good indicator of the proper separation between sugars and non-sugars.

Results of this experiment indicate that the parameters used are more practical compared to those used for Runs #1 to #3. This is supported by the fact that this experiment was run for 14 hours without any drop in the purity of the extract (rather had an upward trend) after the last adjustment in recycle flow rate.

Brix of the products in this experiment showed a definite trend. This is more clear in case of raffinate, after reaching the steady state, it was constant, this is in spite of a higher concentration feed in the latter part of the experiment. However, there was an upward trend for the extract brix, which can be attributed to the higher concentration of the feed in the latter part of the experiment. It can be assumed that concentration of the products is also a good indicator of the separation. If it fluctuates significantly, it is an indication of some problems with the separation in the SMB system.

Experiment Run #5

This experiment was carried out with the molasses which was chemically treated to reduce the hardness as described in materials and methods, but no V.F.F. treatment was applied. This was to study the difference because of filtration treatment on the separation by the SMB system. Composition of feed was also different from the feed used for Runs #1 to #4 (Table 17).

This experiment was started with the parameters of Run #4 with an increased recycle flow rate (Table 8) as it was realized that these parameters are more practical. The results are presented in Figs. 51 to 56.

The rise in the extract purity was not as usual (as in previous runs), it dropped after 2.5 hors, before it reached the steady state (average time is 5 hours). After analyzing the fluid samples from the column bottoms, it was observed that purity in the downward column was higher, thus recycle flow rate was reduced to 250 ml/min as a corrective action. After 5.3 hours, recycle flow rate had to be increased to 280 ml/min, on observing that the purity was higher in upward column. It was observed that pressure on the system was increasing by the time. After 15 hours of the run, pressure had reached to 2.5 bar, whereas it always remained below 2.5 bars in previous runs. After 18.6 hours, recycle flow rate was increased to 290 ml/min to correct the dropping purity. After 25.7 hours, the recycle flow rate

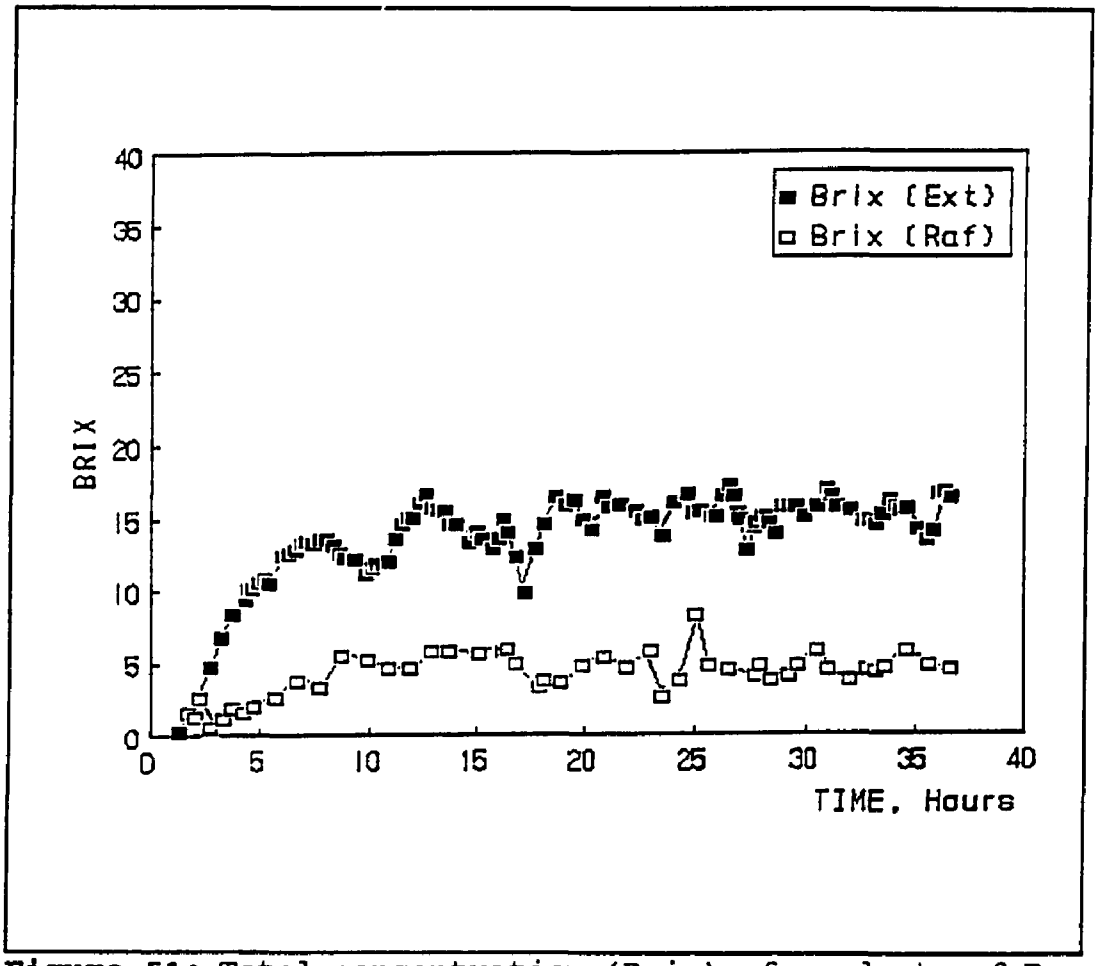

Figure 51: Total concentration (Brix) of products of Run #5.

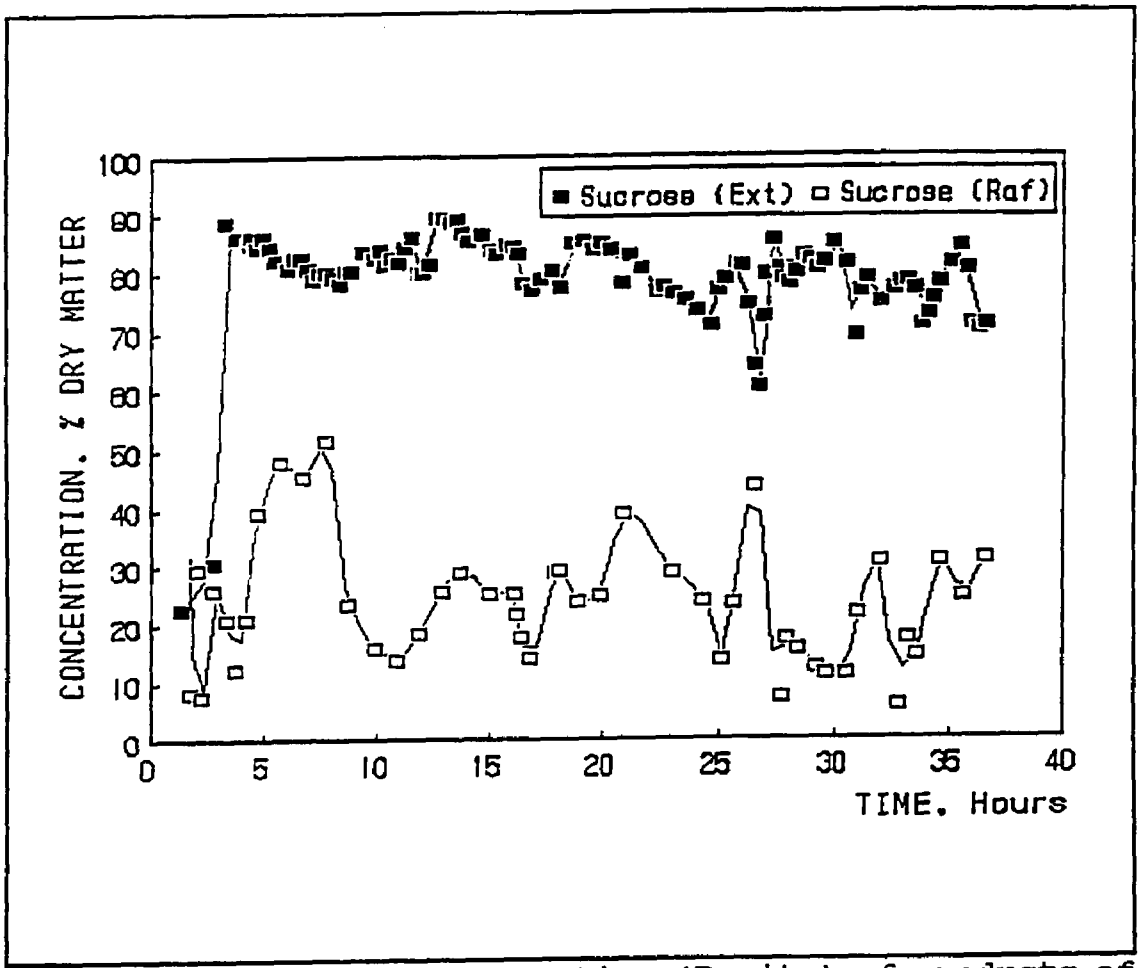

Figure 52: Sucrose concentration (Purity) of products of Run #5.

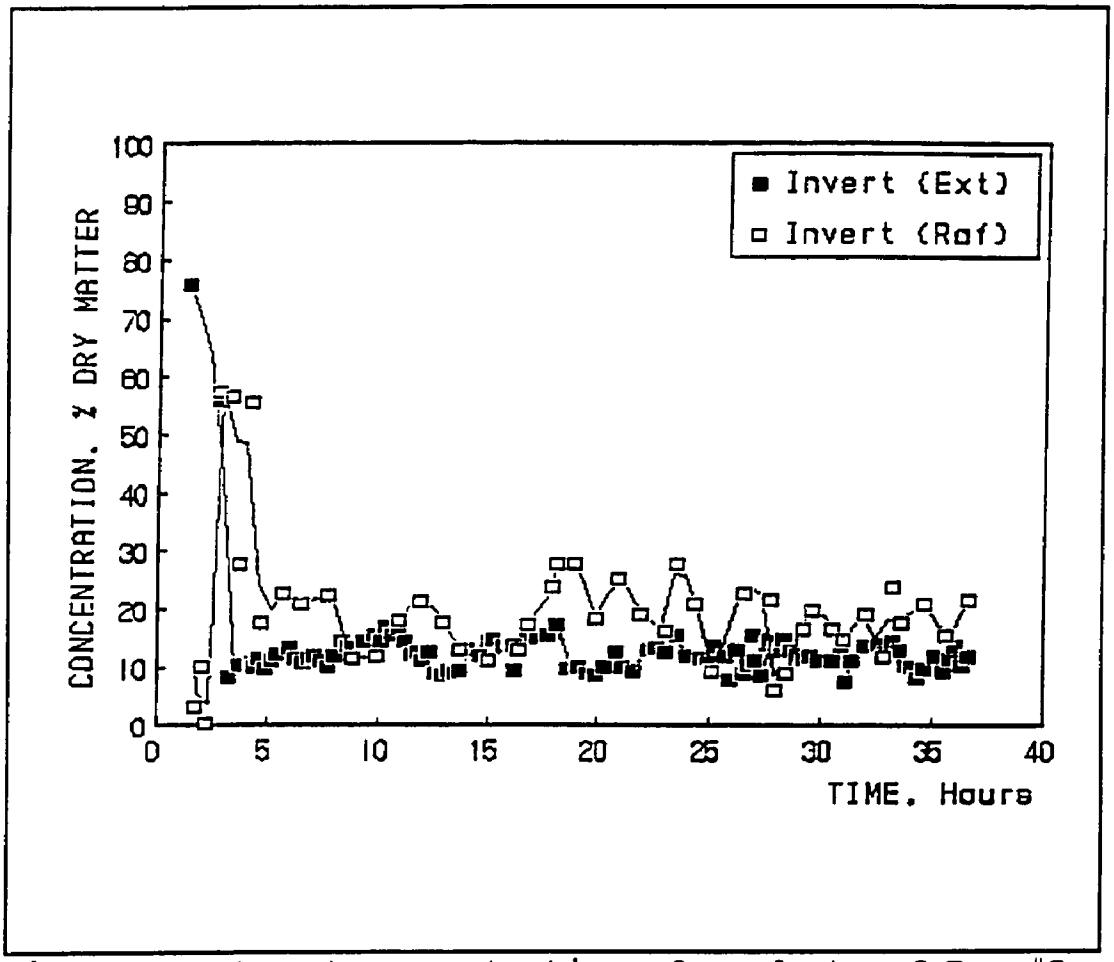

Figure 53: Invert concentration of products of Run #5.

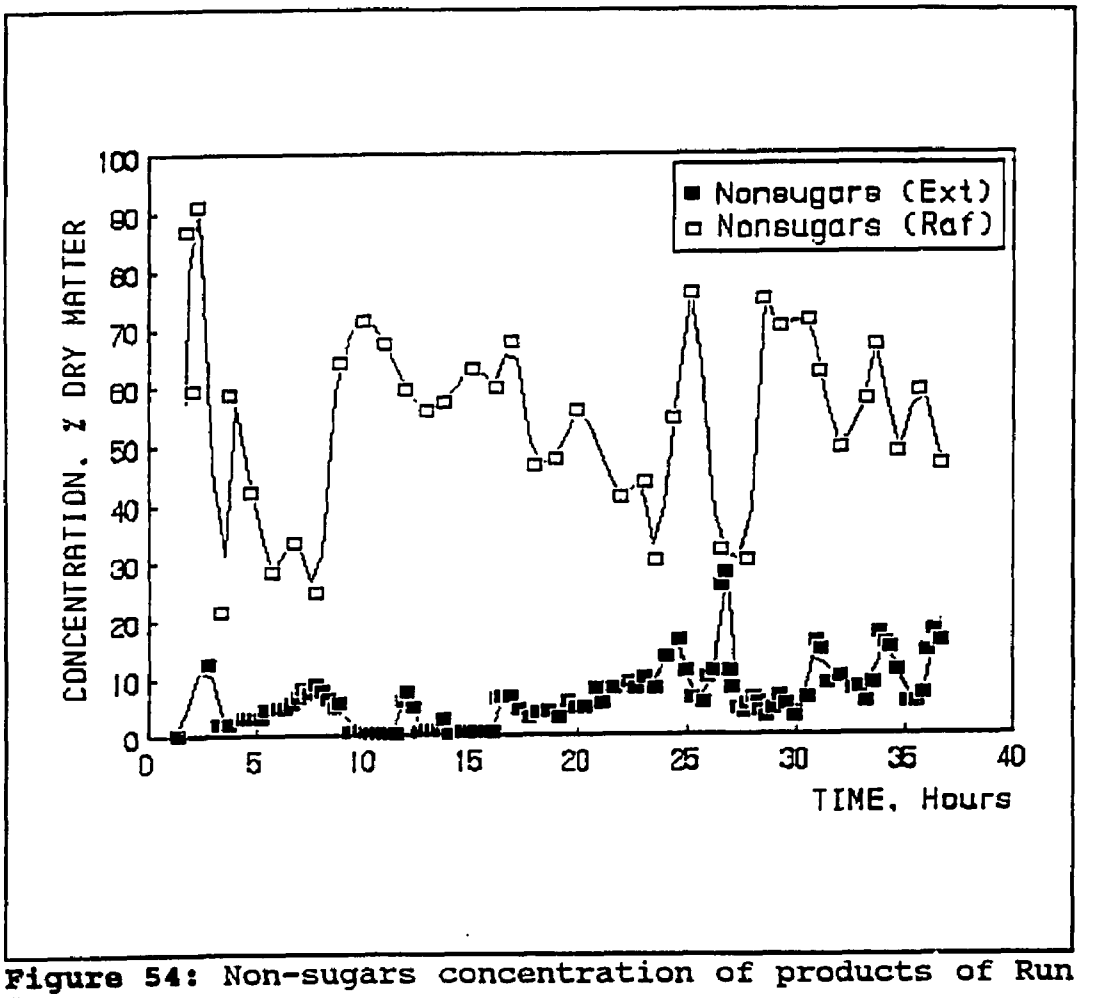

Figure 54: Non-sugars concentration of products of Run #5.

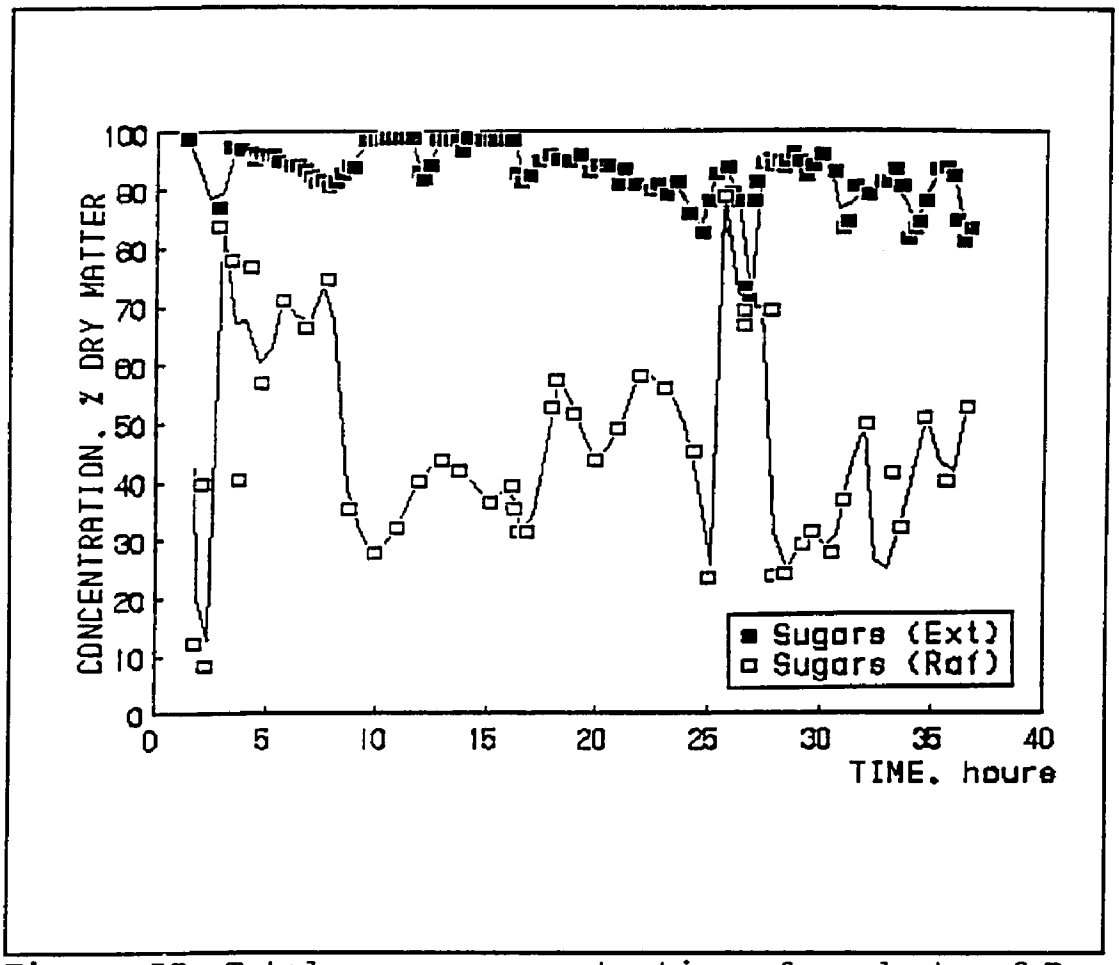

Figure 55: Total sugars concentration of products of Run #5.

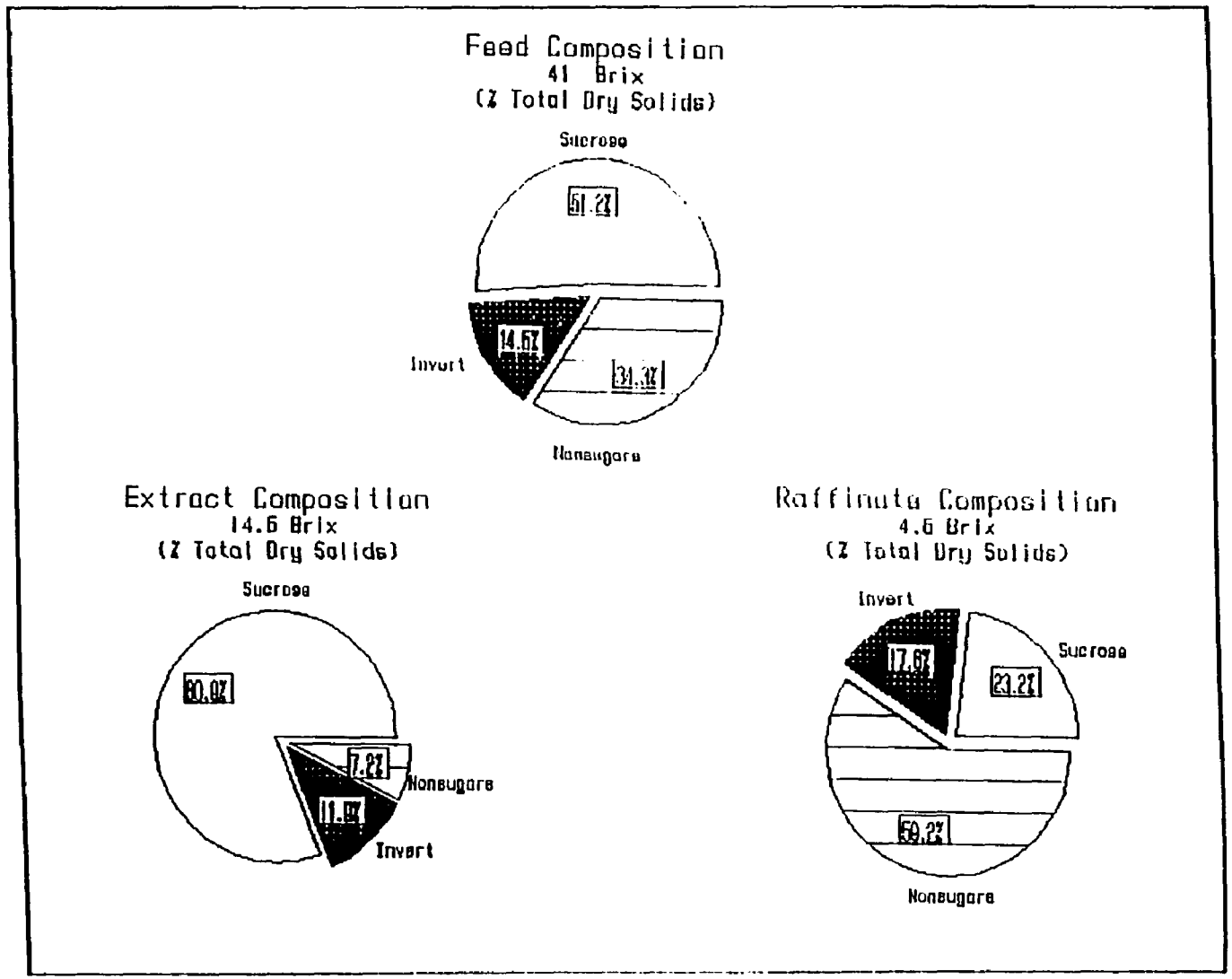

Figure 56: Comparative composition of feed, extract, and raffinate for Run #5.

was reduced to 280 ml/min as corrective action to prevent the purity the extract purity. After 27.5 hours, the purity was again dropped. This time, sequence time was adjusted as corrective action. After 33.25 hours recycle flow rate was increased to 290 ml/min to improve the extract purity. Experiment continued with a fluctuation in the purity value between 70 to 85. Experiment had to be terminated after 36.7 hours, as no more good separation was expected. It was because the pressure on the system had reached 3.5 bar, which was set as working limit on this system. Apparently the pressure was higher because of suspended solids of the feed filled the void of the system that resulted in high pressure. Average composition of the extract and the raffinate is given in Table 26.

Table 26:
Average composition of products Run #5 (on solids).

Products	Bx	Sucrose %	Invert %	Salts %	Sugars %	Color I.U.
Extract	14.5	81.0	11.9	7.2	92.7	35712
Raff.	4.5	23.2	17.6	59.2	40.8	165000

Average purity of the extract is 81.0 and of the raffinate is 23.2. This purity for the extract is the same as for Run #4. The purity of the raffinate is in very high range. While considering total sugars (40.8 %) in the raffinate, it becomes more pronounced that a considerable part of the sugars is in the raffinate. It is evident from the recovery of the sucrose which is 75.5 %, invert 37.7 %

and total sugars only 67.1 %. Again a large part of the invert, about 62.3 %. had gone to the product raffinate.

Concentration of the extract is 34 %, and the raffinate is 10 % of the feed molasses. These values are same as found for Run #4.

Color of the extract is about one third of the feed. The color of the raffinate is much higher than the feed. Overall color is higher in the both products, this is because V.F.F. treatment was not applied to the feed (sec. 5.2.1).

Brix of the products (Fig. 51) show a particular trend similar to that observed for Run #4. Brix, of the both products, was increased gradually and fluctuated somewhat but remained constant throughout the experiment except for the timings when the purity of the extract was dropped considerably.

Comparing the results with Run #4 it is clear that there is a loss of sucrose recovery by 11 %, and 3.2 % more salts has been recovered in the extract, which affects the quality of the extract. About 14.3 % more invert had been recovered into the raffinate. The excessive quantity of the total sugars in the raffinate (40.8 %) can be attributed to the manual control of the pressure at the outlet of the raffinate outlet. To keep the pressure of the system within limits, pressure at raffinate outlet had to be decreased, and at certain stage, it had to keep higher to avoid the

column delivering, not to be dried up. This resulted in a continuous fluctuation (90 to 140 ml/min) in flow rate of the raffinate throughout the run, which eventually affected the separation. When the flow was higher, it is suspected that more sucrose and invert along with salts emerged with the raffinate stream, that made the total sugar percentage higher in raffinate, and reduced the recovery in the extract.

Experiment Run #6

As the parameters of Run #4 were repeated for Run #5, and were found practical, it was decided to increase column load in this experiment while keeping all other parameters same as for Runs #4 & #5. Feed 3, for this run was of 60.5 Brix, more closer to industrial conditions. Based on the experience of Run #5, V.F.F. treatment was applied to Feed 3. Composition of Feed 3 was different from Feed 1 and Feed 2. (Table 17). The results of this run are presented in Figs. 57 to 62.

Compared to previous runs, it took more time before the system reached steady state. It was about seven hours, two hours more that was an average time for the previous runs. This can be attributed to the higher concentration of feed.

The purity rise was as experienced in Run #4, it remained almost stable, after the system reached steady state (Fig. 58). After 11 hours, the purity dropped rapidly

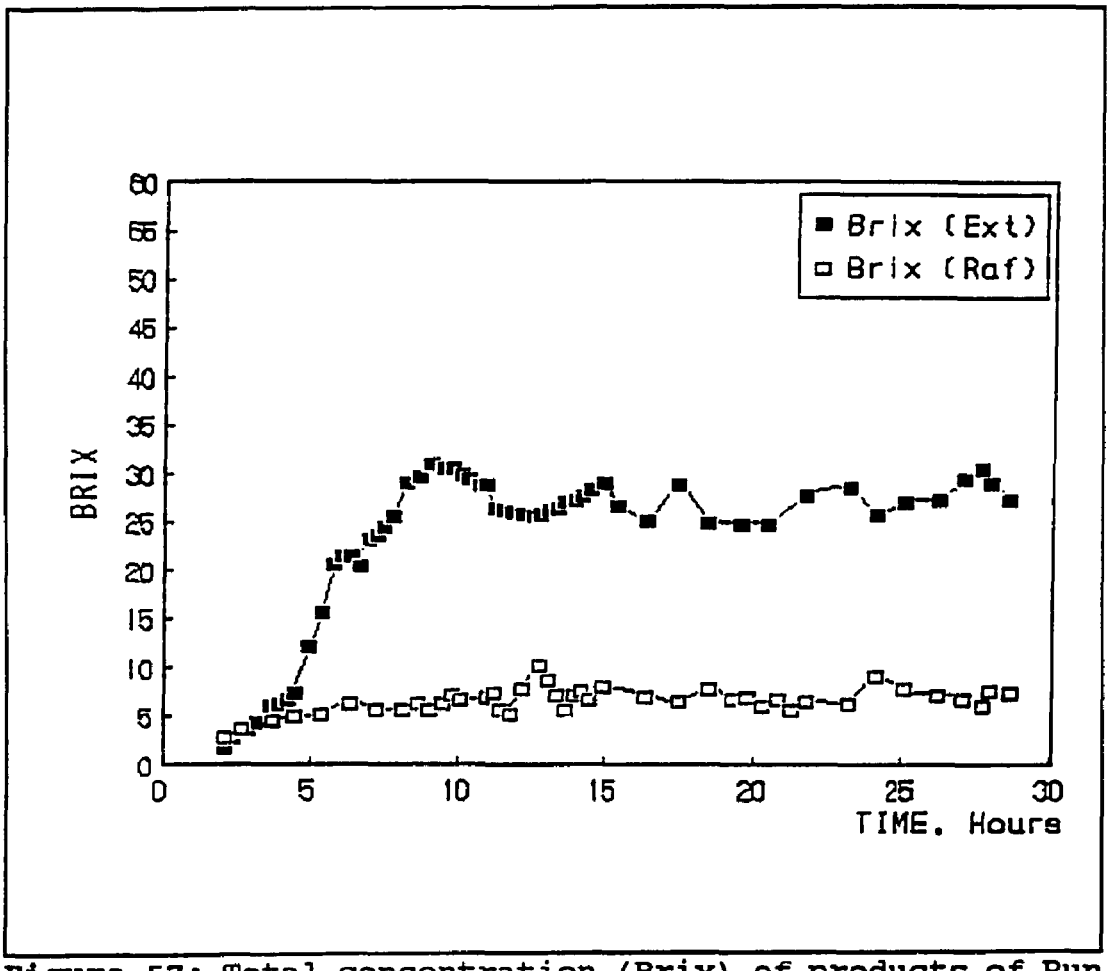

Figure 57: Total concentration (Brix) of products of Run #6.

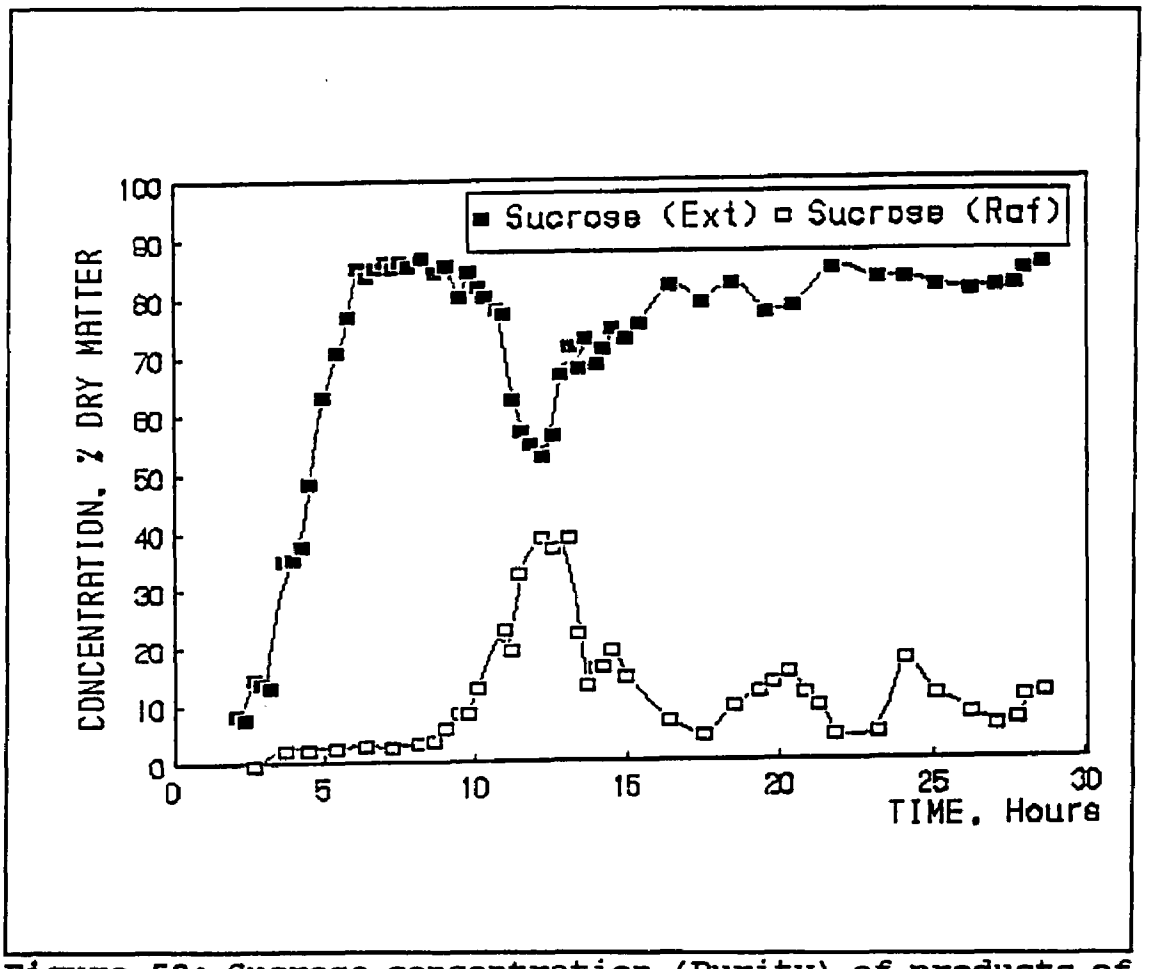

Figure 58: Sucrose concentration (Purity) of products of Run #6.

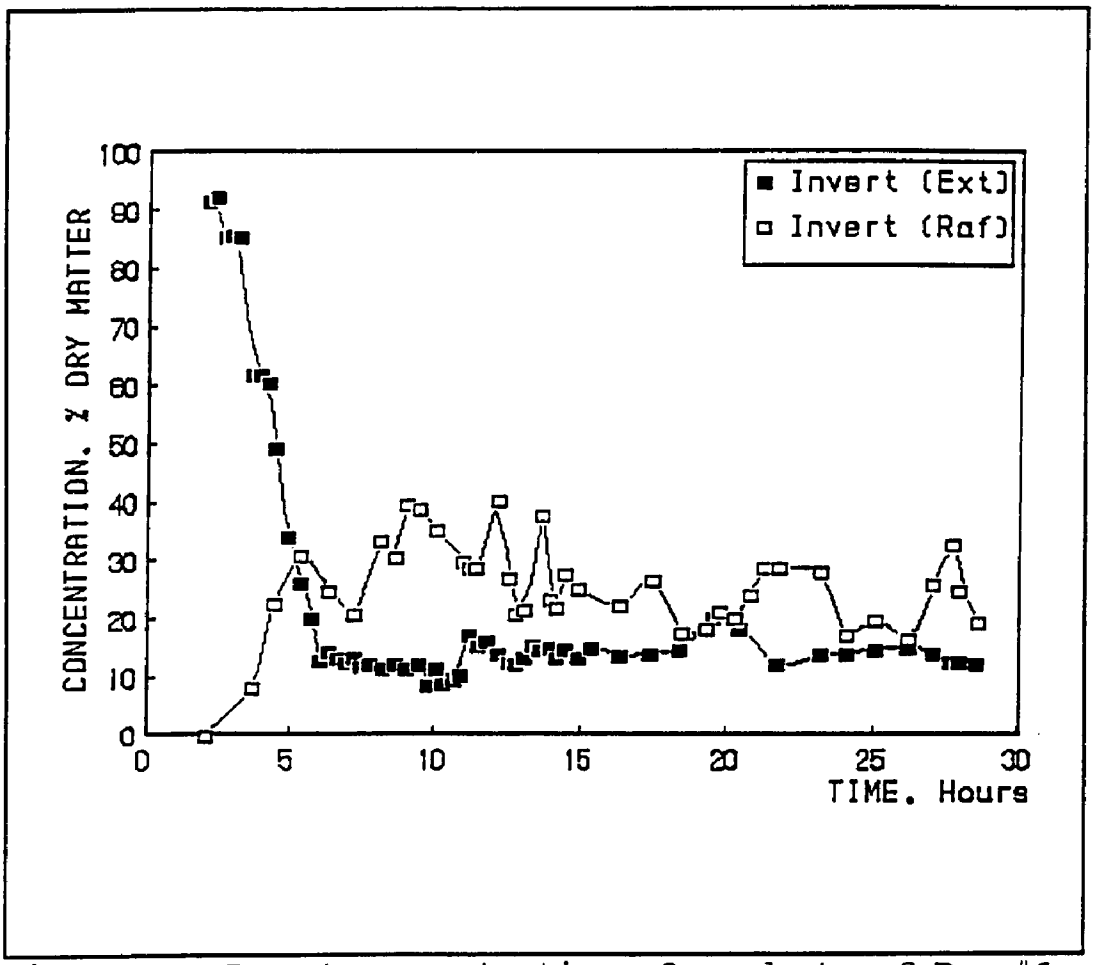

Figure 59: Invert concentration of products of Run #6.

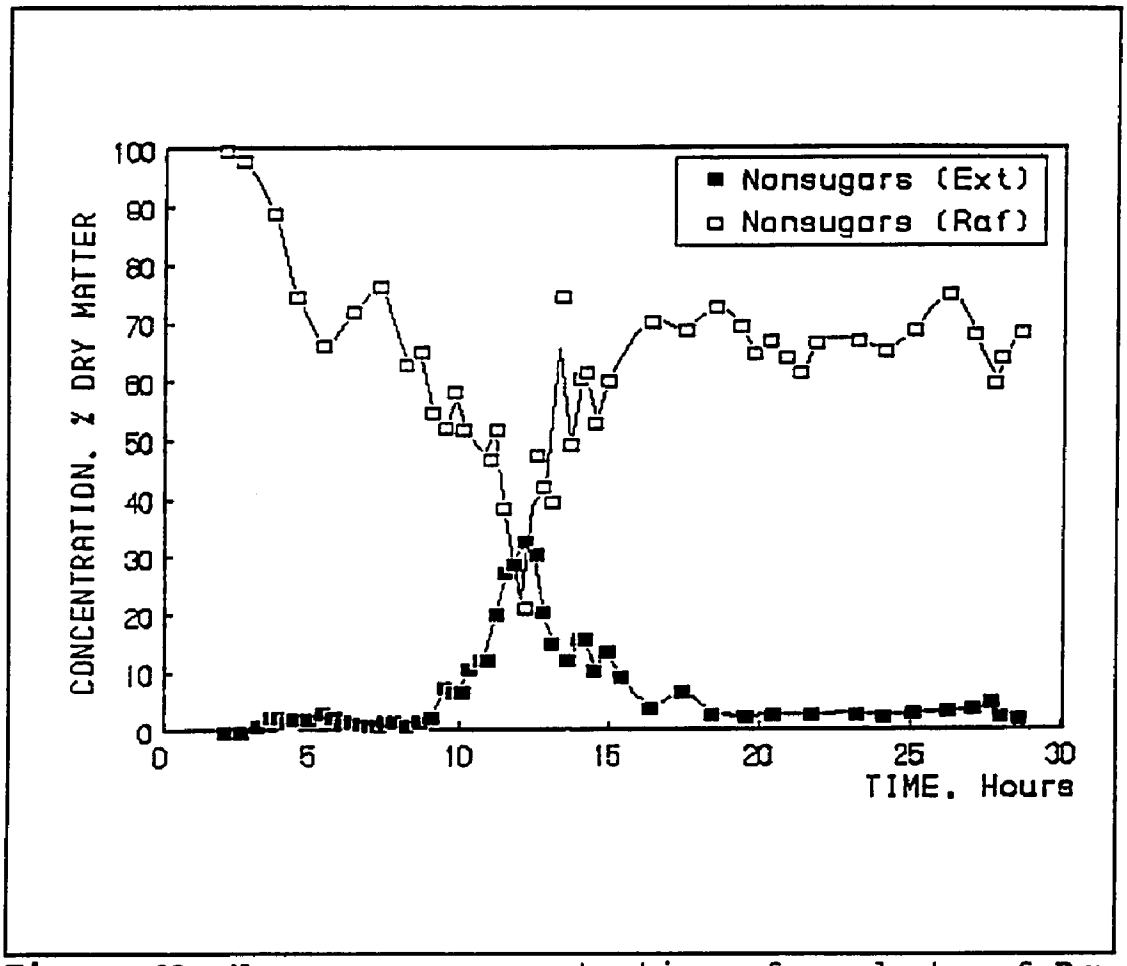

Figure 60: Non-sugars concentration of products of Run #6.

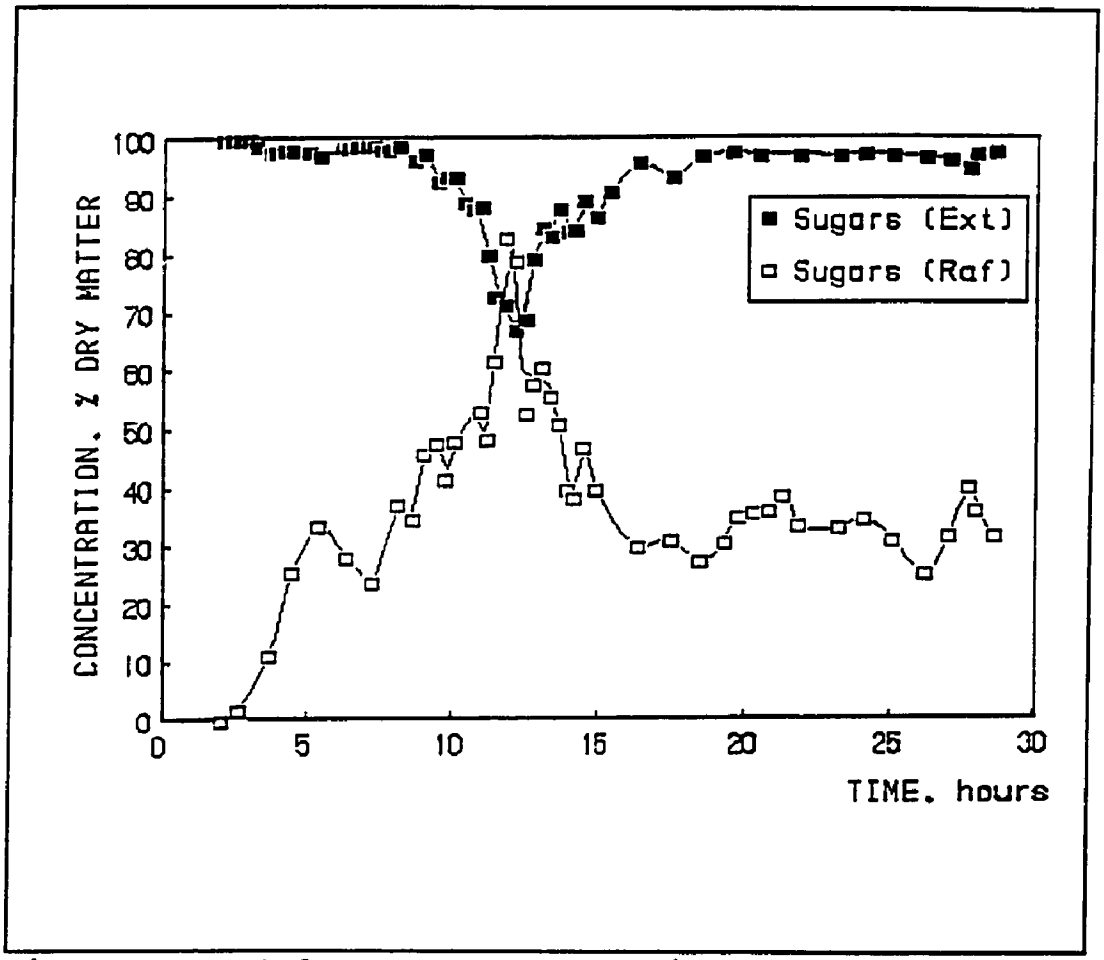

Figure 61: Total sugars concentration of products of Run #6.

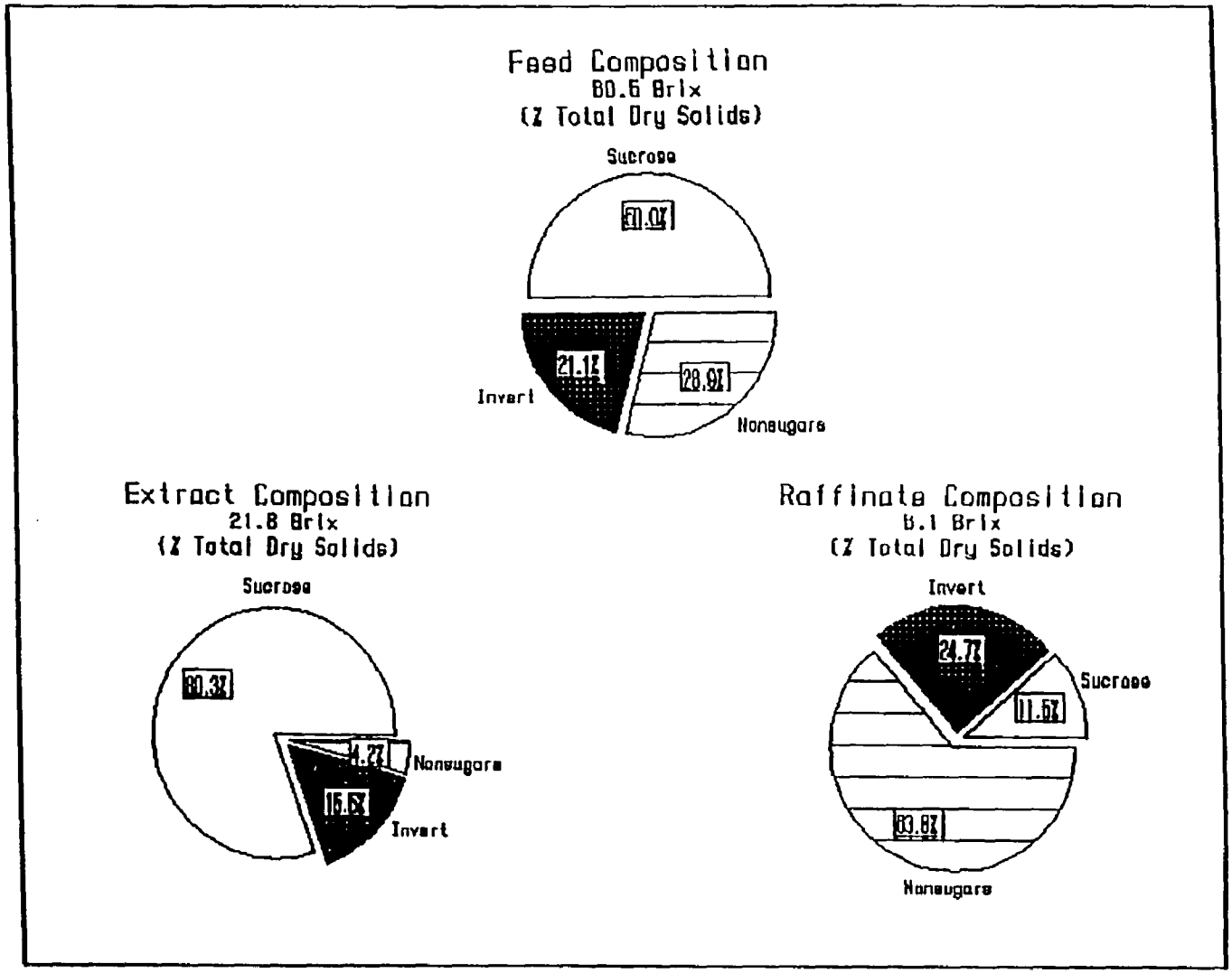

Figure 62: Comparative composition of feed, extract, and raffinate for Run #6.

to about 50. Flow rates of the system were checked with emphasize on water and recycle flow rates, because it was suspected that when system reaches a pressure of 3.5 bar, pumps do not deliver the required volume of the fluids, which leads to drop in the purity. It was discovered that the pressure limits of the system had to be increased to 4.5 (or above if required). After this adjustment in the pressure for the system (after 15 hours), the purity of the extract remained constant within the range of 75 and 85, till the experiment was terminated.

Average composition of the extract and the raffinate is given in the Table 27.

Table 27:
Average composition of the products Run #6 (on solids).

Prod.	Brix	Sucrose %	Invert %	Salts %	Sugars %	Color I.U.
Extr.	21.9	80.3	15.5	4.2	95.8	30550
Raff.	6.1	11.5	24.7	63.8	36.2	112500

The average purity of the extract is 80.3 and of the raffinate is 11.5. These values are similar to those found for Run #4. Whereas the total sugars in the extract and the raffinate are 95.8 and 36.2 respectively. The raffinate contained more sugars compared to Run #4.

Recoveries of sucrose in the extract is above 88 %, invert is 40 %, and salts is 6.5 %. Total sugars recovered in the extract are 79 %. The major part of the sugars in

the raffinate is of invert, on average 60 % invert of feed had gone with the raffinate.

Concentration of the extract is 36 %, and the raffinate is 10 % of the feed molasses. The concentration of the extract is higher than for the previous runs. However, concentration of the raffinate is still very low and need to be increased for commercial purpose.

Color of the extract is about one third of the feed molasses, whereas, the raffinate contained most of the color.

Brix of the products (Fig. 57) in this run was steady except when there was some drop in the purity, or in other words, when the separation was suffering because of less delivery of fluids by the pumps.

A considerable fluctuation in the components of the raffinate (Fig. 59) can be attributed to an uneven flow of the raffinate for the same reason as stated in the experiment Run #5.

Results of this experiment indicate that while working at higher pressure, it is possible to run more concentrated feed. A better purity and recoveries can be achieved with the parameters used for this run provided the other problems related with high pressure can be resolved. This will be discussed in more detail latter.

5.3 General Discussion.

Ion exclusion chromatographic systems combined with simulated moving bed technique are in commercial operation for desugarizing beet molasses, but detailed information is not available in the open literature for the sake of commercial secrecy. Even less information is available for cane molasses.

Comparison of these results with results reported for beet molasses desugarization is questionable. It cannot be assumed that after pretreatment cane molasses is similar to beet molasses. Because beet molasses contain very low hardness and there is negligible invert, and the amount of colorant is also comparatively low, there will be some differences in the results for the both molasses processes in an ion exclusion system.

As the Runs #1 and #3 ended with poor separation, so the results of these experiments are not included in this discussion. The reason of poor separation has been discussed under individual experiment. Though all values has been included in tables and graphs, the average values reported are from Runs #2, #4, #5, and #6. The purity and recovery of sucrose in the extract (high sucrose-low salts product) is the index to monitor the performance of the chromatographic separation system. It will be discussed that how these factors were affected by different conditions of the experiments, which include: purity of the feed,

column loading, hardness in the feed, flow rates within the system, pressure on the system, flow rates of the products. Other than these, general observations regarding the operation of the SMB pilot plant will be discussed.

5.3.1 Purity of the Extract.

Average purity of the extract is between 78 to 81. These values are in close agreement with the value (80-85) reported by Kakihana (1989) working with higher grade molasses, and Munir (1976) who reported a value between 80-85, working with a batch system. Average value is less than 91 reported by Schneider (1978), and 87-94 by Hongisto (1976), but these workers reported their results with batch system on laboratory scale and not with continuous or SMB system at pilot plant. However, the purity of the extract is of course less than what is reported for beet molasses in the literature. This is because beet molasses contain more sucrose, almost no invert and less hardness (Table 1).

It has been reported by Kearney (1990) that for a chromatographic separator purity and recovery are closely related with each other. Higher purity can be achieved at the cost of recovery. It is a matter of choice. There is another limitation for purities beyond a certain range, that is more water will be required to obtain higher purity product. This will yield low concentration products, which will eventually increase a load on the energy system downstream.

(a) Effect of Feed Purity: Tables 28 shows the purity of the feed, extract, and raffinate of Runs #1 to #6. No significant difference can be seen in the purity of the extract. This is in spite of the fact that feed purity for Runs # 2 and #4 is about 44, while the feed purity for Run #5 and #6 is 51.2 and 50.0 respectively.

Table 28:
Purity of the feed and the products (100 * Sucrose/Brix)

	Run #1	Run #2	Run #3	Run #4	Run #5	Run #6
Feed	43.7	43.7	43.7	43.7	51.2	50.0
Extr.	43.5	78.0	75.4	81.0	81.0	80.3
Raff.	63.8	14.3	3.4	10.5	23.2	11.5

(b) Column Loading: Column loading is the term used to specify the quantity of the molasses being introduced to the chromatographic system. There is no standard definition of this term, it has been described in the literature as Kg Non-sugars/m^3 resin/day (Kearney, 1990). In case of beet molasses non-sugars are practically non-sucrose as invert in beet molasses is negligible. In our case, for comparison, we included invert fraction of the molasses in non-sugars. This term basically associated with the capacity of the system. Munir (1976) has suggested column loading in terms of feed purity. He recommended that feed should be of purity 59-61 to avoid any overloading of non-sugars, if purity is below this figure. Of course very low purity molasses could be more problematic at higher nonsugar

loadings. In this study, a column load of 154 kg non-sugars/m^3 resin/day was used in Runs #1 to #5. In case of Run #6, the column load was 220 kg non-sugars/m^3 resin/day. These values are very close to those suggested (160-250 kg non-sugars/m^3 resin/day) by Kearney (1990) for a beet desugarizing plant. No apparent affect on the purity of the extract has been observed.

(c) Effect of residual hardness of feed molasses: The hardness (Ca/Mg as ppm on solids) of the feed molasses for all the runs was in the range of 2500 to 2800. These values are much higher than those reported in the literature (see section 5.3.1). After Run #6 (which lasted for about 30 hours) resin from top of the each column of the SMB system was analyzed. This resin contained 52 mg K, 12 mg Na and 3.6 mg Ca/Mg, all in mg per ml of resin bed. It was found that this adds up to (on average) 2 meq/ml resin capacity, same as found for fresh resin in pure K^+ form. Despite the fact that some ion exchange has taken place, no apparent effect on the extract purity was observed (Table 28). Thus it appears that feed molasses with hardness in the range of 2500 - 2800 ppm can be tolerated by the system without any significant affect on the purity of the extract. This is in contradiction with the findings of Munir (1976), who held responsible the higher ash contents of the feed molasses for the lower purity of the extract. There might be one possibility that all these experiments were run with a very

close range of hardness, so no apparent difference could be observed. If experiment could be carried out with a wide range of hardness, then one may have more information about the effect of residual hardness on the separation in this system. Also a longer experiment is necessary to have information about the effect of ion exchange taking place because of higher value of hardness on separation.

5.3.2: Purity of the Raffinate.

Purity of the raffinate is in the range of 11.5 to 14.3 for Runs #2, #4, & #6. For Run #5 it is about 23 (Table 28). These values are in close agreement to 20 by Hongisto (1979) and 15-18 by Kakihana (1989) while working with cane molasses. Raffinate purity (32 and 20-21) obtained by Schneider (1975), and Hongisto (1979) respectively, for beet molasses is also higher than the purity of raffinate achieved in this study.

The reason for higher purity of the raffinate for Run #5 will be discussed under 'Effect of high pressure on the system. (sec: 5.3.3. d).

5.3.3 Recovery of Sucrose/Sugars in the Extract.

Based on the post treatment of the extract, recovery has been reported in two different forms. Some workers reported sucrose recovered in crystalline form, while the others used the term 'sugars', which includes sucrose and invert.

Recovery of sucrose as well as sugars has been shown in the Tables 15 & 16. It can be seen that average recovery of sucrose for all the runs is between 75.5 and 88.05 % in the extract. The lower value corresponds to Feed 2, without V.F.F. treatment in case of run #5. Average value for runs #2, #4, and #6 corresponds to 78.5 % sucrose recovered in crystalline form. This assumption is based on 90 % recovery of sucrose through conventional crystallization (Munir, 1976; Hongisto & Heikkila, 1978). Average values of sugars recovered are 67.1% for Run #5 and 78.4% for Runs #2, #4, and #6. The values obtained for sucrose recovery in this work are superior to those reported by Zievers (1974), Schneider (1978), and Hongisto and Heikkila (1978). Average values are lower than those reported by Gross (1971), Munir (1976) and by Hongisto (1979). All these workers used batch type system on laboratory scale. These values are in close agreement with Kakihana (1989) working with higher grades molasses on SMB system. All these values are lower that those reported by Kearney (1990) and Chertudi (1991) for beet molasses while working on SMB ion exclusion system on commercial scale.

(a) Effect of feed purity: No significant effect can be seen on the recovery of sucrose/sugars because of difference in feed purity in case of Runs #2, #4, and #6. Though recovery values are lower for Run #5 but this can not be related to the feed purity as it was almost same to that

used for Run #6. Though it has been suggested that as the feed purity increases, the sucrose recovery should be higher (Kearney, 1990 A) but we see no apparent effect of higher purity on sucrose recovery for Run #6.

(b) Column loading: As discussed before, column loading describes how much solids are being fed to the separator. Column loading is based on the capacity of the resin, and thus can not exceeds a certain range. No apparent detrimental effect can be seen because of different (154 & 220 kg non-sugars/m^3 resin/day for Runs #1 to #5 and Run #6 respectively) column loadings in this study. There is no information available in the literature about the effect of column loading on the recovery of sugars in the extract, however Kearney (1990) suggested 140-250 kg non-sugars/m^3 resin/day as working range on commercial scale.

(c) Effect of residual hardness: As discussed before feed molasses used in this study has a close range of hardness. For this range, we see no significant on recovery of sugars. For Runs #2, #4, and #5, the residual hardness in the feed molasses was almost the same i.e 2800 ppm, but there is significant difference in sugar recovery, so hardness can not be held responsible for lower recovery in case of Run #5.

(d) Effect of higher pressure on the system: In case of Runs #1 to #4 the working pressure of the system remained below 3 bars. In case of Runs #5 and #6, the pressure

exceeded this limit. For Run #5, feed used was without V.F.F. treatment, thus contained soluble solids and some form of colloidal, which filled up the voids of the system and led to the development of high pressure on the system. To keep the pressure within the set limits, there is only one choice, under the present arrangements, and that is to control the pressure on the raffinate outlet. It was because when pressure at this point was reduced to minimum, the raffinate flow was increased and then in order to avoid the column delivering raffinate from being dried out, pressure had to be increased to decrease raffinate flow. Raffinate flow was affected significantly by controlling the pressure from this point. Raffinate flow fluctuated between 85 and 120 ml/min. throughout the experiment. It affected the separation operation in many ways.

a) It caused unnecessary accumulation of non-sugars onto the system in one time (in case of slow flow of raffinate), and excessive flow sugars towards raffinate exit, in other time.

b) It resulted negative pressure on the column delivering the recycle stream which caused suction of air (by leakage) from the top connections of the column. This air remained in the system and spreaded across the eight columns. It reduced the efficiency of the resin by channeling for the components and reducing the chances of contact with resin.

c) At each switch change to next column/s, there was no flow of liquid for a certain time, to the column delivering

recycle (through the pump). This was because the pressure (about 3.5 bars on this column, while it was recipient of recycle stream), was higher than the column upstream. It took 20-30 seconds to dissipitate that pressure right after the switch change and flow of liquid from the upstream was restored.

d) High pressure on the system reduced the capacity of the pumps, specially recycle and water pumps, delivering liquid to the column with maximum pressure. This eventually led to reduced flow of fluids in the different zones of the system affecting the movement of different components in different zones.

It was discovered during Run #6, that pressure limit of the system to be increased in order to have required flow rates of different streams in respective zones. So, 4.5 bars was set as upper limit and it was found that pumps are delivering required flow rates as per calculations/setting. Thus lower recovery for Run #5 can be attributed to the reduced recycle flow within the system and no other factor such as feed purity, or column loading can be held responsible. Absence of V.F.F. treatment can be an indirect cause of this problem as suspended solids and colloidal filled up the voids of the system and led to high pressure development.

5.3.4 Concentration of the Products.

Concentration of the products is one of the most important factor of the desugarizing of molasses operation. Dilution of the separated fractions is a major concern for commercial application of this system. To evaporate the extra water for post handling requires excessive amount of steam resulting an increased load on the energy sources. This was one of the reasons, why conventional chromatography could not be applied in the industry. It was experienced that simulated moving bed chromatographic system results in less diluted products as less eluent is required for operation compared to fixed bed systems (Table 2).

Performance of the SMB ion exclusion system is judged by the dilution of the products as well. Dilution of the products is a function of the feed concentration and the amount of eluent required for optimum separation.
This can be explained by elution water/feed molasses (W/M) ratio. The higher W/M ratio will be, the more diluted products will result. No doubt that more the eluent is used the higher purity of the extract will be. This should not exceed certain limits to avoid unnecessary dilution of the products to minimize the load on energy sources.

Concentration of the products expressed as Brix (Bx) for all the runs and concentration % of feed molasses are shown in Tables 29 & 30.

Though the (volumetric) ratio of water and feed molasses is same for all the runs, but based on solids, this is 5.2 for Runs #1 to #5 and 4.6 for Run #6.

Table 29:
Concentration of feed and products (Bx).

	Run #1	Run #2	Run #3	Run #4	Run #5	Run #6
Feed	40.5	40.5	40.5	40.5	41.0	60.5
Extr.	11.8	9.8	7.9	13.9	14.5	21.9
Raff.	2.9	2.3	0.8	4.1	4.5	6.1

Table 30:
Concentration % feed.

	Run #1	Run #2	Run #3	Run #4	Run #5	Run #6
Extr.	29.14	24.3	19.50	33.0	34.0	36.0
Raff.	7.16	5.7	19.7	9.5	10.1	10.0

For Runs #2, #4, #5, and #6, the average Bx of the extract is 9.8 to 21.9 and concentration % feed is 24.3 to 36 %. For the raffinate, Bx values range between 2.3 to 6.1 and concentration % feed is between 5.7 to 10.1.

For extract, these values are in good agreement with those reported by Gross (1971), Zeivers (1974), Schneider & Mikule (1975), Hongisto and Heikkila (1978), but are lower than those reported by Hongisto (1976), Kakihana (1989), and Chertudi (1991). For raffinate, the values found in this work are lower than those reported by Schneider & Mikule (1975), Hongisto and Heikkila (1978), Kakihana (1989), and Chertudi (1991). No other researcher reported the Bx values of the raffinate.

As mentioned earlier, dilution is associated with the purity of the products, thus no generalization can be made in this respect. Decisions depend basically on the post treatment of the separated fractions.

It can be seen that after the system reached steady state (Figs. 27,33,45,51 and 57), the Bx curve for both the extract and raffinate show a particular trend, that is concentration is constant, it dropped only when separation was upset for any reason. It can be assumed that concentration can be a good indicator of separation performance. Even in the absence of other analytical techniques such as HPLC analysis of the products, concentration of the products gives good information about the separation operation.

5.3.5 Effect of Velocity Changes on Separation.

Based on the assumptions made to design the system,(sec. 2.3.3) when feed is introduced at the beginning of zone II (Fig. 6), non-sugars should move faster than the port movement in zone II, and zone II and move slower in zone I, such that non-sugars are moving downstream in zones II, and III, and upstream in zone I. Sucrose should move slower than the port movement in zone II, and III, and move faster in zone IV. To have an optimum separation, fluid flow rates in respective zones should be adjusted such as that all conditions required as discussed above are fulfilled.

$$V_{solid} = 1 \text{ column} / time_{column} = V_{resin} \quad (5.1)$$

Though number of columns per zone are different, the actual movement of resin is one column per switch time. The conditions (Table 8) for Runs #2, #4, #5, and #6 will be discussed first.

$$V_{resin} = 210 \text{ cm} / 8.6 \text{ min} = 24.42 \text{ cm/min.} \quad (5.2)$$

where
1 port = Length of a column = 210 cm
time port = switch time (S.T.)= 8.6 min

To calculate the velocity of the individual component the following expression was used (Ruthven, 1986).

$$v = \frac{V_{fluid}}{1 + \frac{1 - \epsilon}{\epsilon} * K} \quad (5.3)$$

where
v = velocity of the component in the system,
V_{fluid} = interstitial velocity of the fluid in the zone,
ϵ = void volume of the system, and
K = Distribution coefficient of the component.

Interstitial velocity of the fluids in the respective zones is calculated from the volumetric flow rates adjusted based on the assumptions made in material and methods (sec. 4.2.2). Flow of fluids (volumetric and interstitial) in each zone is given here:

	Volumetric flow rate	Interstitial velocity
Zone I =	280 ml/min	24.15 cm/min
Zone II =	390 ml/min	33.64 cm/min
Zone III =	370 ml/min	31.92 cm/min
Zone IV =	400 ml/min	34.50 cm/min

Velocity of sucrose, invert and non-sugars in each zone as calculated using following values for K. ($K_{Nonsugars}$, 50%= 0.00; 50%= K_{KCl}= 0.25; $K_{sucrose}$= 0.33; and K_{Invert}= 0.48) by equation (5.3) are:

	Zone I	Zone II	Zone III	Zone IV
$v_{sucrose}$ cm/min	16.37	22.81	21.64	23.39
$v_{non\text{-}sug}$ cm/min	20.95	29.19	27.69	29.94
v_{invert} cm/min	34.50	19.89	18.88	20.42

It can be seen that conditions to have proper separation between sucrose and non-sugars as discussed above were met as:

for sucrose:

In zone II and III: $v_{sucrose} < V_{resin}$ (5.4)

zone II 22.81 < 24.42

zone III 21.64 < 24.42

and in zone IV: $v_{sucrose} > V_{resin}$ (5.5)

zone IV 29.94 > 24.42

and for non-sugars:

In zone II and III: $v_{Non\text{-}sugars} > V_{resin}$ (5.6)

zone II 29.19 > 24.42

zone III 27.19 > 24.42

and in zone I: $v_{Non\text{-}sugars} < V_{resin}$ (5.7)

zone I 20.95 < 24.42

It can be seen that for Runs #2, #4, #5, and #6, the flow rates were appropriate and matched with switch time, that is why these runs ended with good separation.

For Run #1 (switch time = 8.6 min) flow of fluids (volumetric and interstitial) in each zone were as follows:

	Volumetric flow rate	Interstitial velocity
Zone I	218 ml/min	18.80 cm/min
Zone II	328 ml/min	28.29 cm/min
Zone III	308 ml/min	26.57 cm/min
Zone IV	338 ml/min	29.15 cm/min

Velocity of sucrose and non-sugars in each zone as calculated by eq. 5.3 are:

	Zone I	Zone II	Zone III	Zone IV
$v_{sucrose}$ cm/min	12.75	19.18	18.01	19.76
$v_{non\text{-}sug}$ cm/min	16.31	24.55	23.05	25.29

It can be seen that the conditions to have proper separation were not fulfilled in this run and that is why this run ended with poor separation.

for sucrose:

zone II 19.18 < 24.42 (as per eq. 5.4)

zone II 18.01 < 24.42

zone IV 19.76 $\not<$ 24.42 (not as per eq. 5.5)

for non-sugars:

zone II 24.55 > 24.42 (as per eq. 5.6)

zone III 23.05 $\not>$ 24.42 (not as per eq.5.6)

zone I 16.31 < 24.42 (as per eq. 5.7)

For Run #3 (switch time = 18 min), flow of fluids (volumetric and interstitial) in each zone were as follows:

	Volumetric flow rate	Interstitial velocity
Zone I =	50 ml/min	4.31 cm/min
Zone II =	160 ml/min	13.80 cm/min
Zone III =	140 ml/min	12.07 cm/min
Zone IV =	170 ml/min	14.66 cm/min

Velocity of sucrose and non-sugars in each zone as calculated by equation (5.3) is:

	Zone I	Zone II	Zone III	Zone IV
$v_{sucrose}$ cm/min	2.92	9.35	8.18	9.94
$v_{Non\text{-}sug}$ cm/min	3.74	11.97	10.47	12.72

It can be seen that like Run #1, conditions for proper separation were not fulfilled in this run, that is why this run ended with poor separation.

(V_{resin} = 210 cm / 18 min = 11.66 cm/min)

for sucrose:

zone II 9.35 < 11.66 (as per eq. 5.4)

zone III 8.18 < 11.66

zone IV 9.4 $\not<$ 11.66 (not as per eq.5.5)

for non-sugars:

zone II 11.97 > 11.66 (as per eq. 5.6)

zone III 10.47 $\not>$ 11.66 (not as per eq. 5.6)

zone I 3.74 < 11.66 (as per eq. 5.7)

It can be seen that conditions of movement of sugars and non-sugars were not met in this run and this resulted in poor separation.

Partitioning of invert in the products of SMB system:

We have discussed the effect of fluid velocity on separation of the two major components of the molasses, i.e. sucrose and nonsugars. Third major component of the molasses, the invert was partitioned unevenly between the both products, 40% of the invert had gone with the extract and 60% with the raffinate.

Conditions for invert to go with sucrose:

In zone II and III: $v_{invert} < v_{resin}$

zone II 19.89 < 24.42 (as per eq. 5.4)

zone III 18.88 < 24.42

and in zone IV $v_{invert} > v_{resin}$

zone IV 20.40 $\not>$ 24.42 (not as per eq. 5.5)

Condition for invert to go with nonsugars:

In zone II and III $v_{invert} > v_{resin}$

zone II 19.88 $\not>$ 24.42 (not as per eq. 5.6)

zone III 18.88 $\not>$ 24.42 (not as per eq. 5.6)

and in zone I $v_{invert} < v_{resin}$

zone I 34.50 $\not<$ 24.42 (not as per eq. 5.7)

As can be seen from the calculations, conditions were neither fulfilled for invert to go with sucrose nor to go with nonsugars fraction. In zones IV, the velocity of the invert was less than the velocity of the resin, whereas to

go with sucrose it should be higher. In zones II and III, the velocity of the invert was less than the velocity of the resin, and in zone I velocity of invert was higher than than the resin velocity, thus conditions to go with nonsugars were not met. That is why the invert was partitioned unevenly between the both products. This was because in this study, the SMB system was designed (and operated) to recover maximum sucrose from molasses in high sugar stream, the extract. In order to recover the invert as a separate product, the system needs to be modified and operation to be redesigned, only then the losses of sugars in the raffinate stream can be reduced.

It was suggested (Kearney, 1990) that by selecting proper flow rates and switch time, a steady state profile within the system can be achieved. This profile moves around the system and is the basis of this process, which helps to reduce the inventory of resin as well as eluent required optimum separation. In case of Run #1 and #3, it is clear that steady state profiles can not be maintained throughout the experiment. By the experience gained from these experiments, a higher recycle flow rate was tried in later runs which proved to be appropriate for optimum separation. However, the flow rates tried in these experiments can not be claimed as final or optimum for commercial operation. More work is suggested to optimize

these parameters to have enhanced purity and recovery of sucrose in the extract.

5.3.6 Microbial Growth on the System.

The working temperature of the system was 70°C, that is the column were maintained at this temperature, but there are some cold spots such as tops and bottoms of the columns, piping, pumps, feed and extraction loops. These spots are exposed to room temperature all the time. There seems to be no problem when the system is in operation, but when it is stopped for any reason, or for an overnight break, the risk of microbial growth is always there. The main problem of bacterial growth arises from the recycle stream, which is exposed to room temperature during any break, and because of low dilution of sugars (Bx 1-2) in the recycle (out of the columns, in loop and piping), growth of the bacteria and yeast takes place, and on re-starting the operation it is circulated throughout the system. It seems that, this thermo-resistant yeast survives at 70 °C, and thus sticks to the walls and resin in the system. After Run #5, photographs of the resin indicated accumulation of some foreign material on the resin, which is believed to be microbial colonies. It was intensified in case of Run #5, as feed used was not filtered properly, so it is assumed that some material from the molasses accumulated onto the resin and resulted in extensive growth of microbes thereon.

Some smell in the extract stream was noticed when experiment is started after overnight break, which vanishes after 30-45 minutes of operation. Samples of the feed (after the pump), extract and raffinate (after 15 minutes of operation) on the 2nd last day of Run #6 were analyzed for bacteria and yeast by Standard Plate Count (SPC) method. Results of analysis are presented in Table 31.

Table 31:
Microbial count in feed, extract, and raffinate (Run #6).

	Bacteria/ml	Yeast/ml
Feed	2.05×10^5	1.11×10^3
Extract	3.60×10^7	4.0×10^6
Raffinate	6.40×10^6	1.0×10^5

Bacteria detected were gram + cocci. For extract, an increase in numbers of bacteria and yeast was observed by (about) 2 log cycles and 3 log cycles, respectively. For raffinate, increase in number of bacterial and yeast was by 1 log cycle.

Higher values for the extract can be explained as: Flow rate of the extract is 30 ml/min, thus it takes longer time (about 20 minutes) from bottom of the column to reach the collection point. Immediately after leaving the column, it is exposed to room temperature. Other reason is that it contains more sugar (over 80 %) and is of reasonable concentration (15-25 Bx), thus conditions for the growth of bacteria and yeast becomes favorable. In case of raffinate as the flow is higher (110 ml/min) it takes about 4-5

minutes to reach collection point, so the temperature of the product is always close to 70 °C.

It is believed that by increasing the temperature of the system above 75 °C, this problem can be minimized. It has been suggested to run the system at higher temperatures (about 80 °C and even 90 °C) to avoid any kind of microbial growth (Munir, 1976; Hongisto, 1976; Aguirre, 1982; and Kearney, 1990). Resin might have some limitations because of adverse effect of higher temperature on its mechanical stability, but now resin are available in the market which can withstand higher temperatures. Working temperature range for the resin, used in this study, is 25 -90 °C as recommended by the manufacturer. There is another option, which is similar to industrial conditions, the system should be run continuously as long as possible. There should be no overnight break at least, thus chances of development of microbial growth will be minimal. In this case the adverse effects of increased temperature on the sucrose such as caramelization can be avoided.

5.3.7 Post-treatment of the Products.

(a) Decolorization of the Extract:

Decolorization of the extract was carried out as described in the material and methods (sec 4.2.5). Composite sample from the extract for Runs #6 was decolorized. Samples after passing each column were

analyzed for concentration, pH, and color. Results are presented in Table 32.

The color of the extract was reduced from 30550 I.U. to 420 I.U. by passing through four columns as mentioned below. It is in agreement with those reported by Hongisto (1977) and others.

Table 32:
Decolorization of extract from Run #6.

Column	Brix	pH	Abs_{420}	Color, I.U.
Column #1	5.3*	7.26	0.65	12000
Column #2	17.9	2.63	0.65	3380
Column #3	15.4	2.72	0.13	794
Column #4	11.4	9.74	0.05	420

Note: 4 samples each of 500 ml, were analyzed after exiting from each column. Results presented are average of 4 samples. (* is the brix at which color was measured)

(b) Crystallization of Extract:

Conventional industrial crystallization procedure was applied to crystallize the sucrose contents of the extract. Unfortunately, due to limitations of the available facilities (the quantity of the extract was not enough) this objective could not be achieved. We had to wait till enough quantity can be obtained from the system. Latter because of shortage of time this could not be done. However, assumptions can be made based on the theoretical yield of granulated sucrose from the extract.

Chapter 6

CONCLUSIONS AND RECOMMENDATIONS

Since several aspects are involved in this study, the following conclusions are offered in separate sections as outlined below:

- Characterization of resin by pulse testing technique.
- Separation of cane molasses on SMB pilot plant.

Characterization of Resin:

Pulse Testing: Pulse testing procedure, on pilot plant itself, proved to be helpful to determine the characteristics of the resin to be used for separation of molasses. This provided information such as isotherms (& distribution coefficient) and kinetics of the system, which lead to design the SMB operation.

Dowex Monosphere 99 CA Resin (Ca^{++} form):

Glucose and fructose isotherms were found to be nonlinear and coupled. The differential adsorbed amount of solutes increased with increase in solution concentration. This behavior is likely due to an increasing dehydration of the solute and adsorbent surface by an increase in solution concentration.

XUS 40166.00 Resin (K^{+} form):

The same mechanism as of separation of glucose and fructose on Ca^{++} form resin, observed for sugars indicated that it is independent of ionic form of resin. Interaction

of potassium chloride and sucrose affecting the adsorbence of sucrose was observed. Potassium chloride showed a different behavior, at higher concentrations (above 8 g/l) it was increasingly adsorbed onto the column.

For a successful modeling of the SMB operation, cane molasses should be considered as five component mixture of sucrose, glucose, fructose, potassium chloride, and non-retained fraction (K=0).

Separation of cane molasses by SMB pilot plant:

The Simulated Moving Bed Ion Exclusion System was used successfully to separate the cane molasses and produce Extract, and Raffinate within acceptible purities and recovery. Purities of 96% for total sugars and 81% for sucrose were achieved. Up to 79% of total sugars and 88% of sucrose were recovered in extract.

Column loading of 220 kg non-sugars/m^3/day was used successfully without any significant affect on separation in terms of purity of the extract and recovery of the sugars.

Product concentration of up to 22 Brix for the extract and 6.1 for the raffinate were achieved.

Color of the extract was reduced, after decolorization, by a factor of 190, (of the feed molasses). This reduction in color includes the effect of SMB operation as well. The reduction in color is more than satisfactory, however, a drastic drop in pH while passing through the columns #2 (Resin: XA100/1) poses a serious threat to the sucrose

contents of the product. At this low pH, sucrose is likely hydrolyze to invert. If decolorization by this method is to be adopted it should be done at low temperature. This treatment on ion exchange with the resins used in this study need further investigation.

Residual hardness (Ca/Mg 2500-2800 ppm on solids) of molasses proved to be acceptable without any significant affect on the separation performance of the system. However longer experiments are needed to see how long this range of hardness can yield acceptable results in industrial conditions.

SMB Ion Exclusion system could be useful in meeting the commercial needs of sugarcane industry since extract of over 81% purity was obtained at product scale throughput. The extract can be combined with clarified juice stream or with syrup after evaporation. The raffinate disposal depends upon certain conditions. It could be concentrated and mixed with cattle feed as its energy value is still high because of presence of sugars as up to 37%. However, the disposal of raffinate is still a problem yet to be solved.

Since the system is yet to be optimized, it is not possible to do an economic analysis of the process at this stage. However, as long as the sugar world market prices are low , economics of this process is highly dependent on local conditions, price of raw sugar and molasses. A detailed cost evaluation should be performed according to

the local conditions to establish the economic feasibility of this process.

It is understood that suitability of molasses for SMB process will depend on quality of factory clarification. Some considerations should be given to molasses quality when purchased for this process. Some kind of arrangements for a premium/penalty on molasses for Ca^{2+}/Mg^{2+} levels and/or for sucrose contents can lead to economically practical operation of the SMB system.

Recommendation for future work:

Residual hardness of the molasses used in this study was of very limited range, thus no significant effect could be observed. It is suggested that a wide range of hardness be tested for validation of the process on a industrial scale.

Invert was partitioned between the extract and raffinate at 40% and 60 %, respectively. This behavior caused high concentration of total sugars in raffinate. This could be reduced by designing the system such as to recover invert as a separate product without effecting the separation of sugars and non-sugars.

It is believed that in spite of reasonable purities and recoveries of the extract and raffinate reached in this study, still more work is needed to be done to optimize the separation parameters to meet the industrial conditions. Concentration of the products must be considered as the cost

of evaporation can be a significant factor in commercialization of this process.

Another area of concern is microbial growth on the system. To avoid this, it is recommended that future experiments be designed on a no-stoppage basis. This will be a more realistic approach to predict the results on industrial conditions. Periodic analysis of feed and products for microbial study is also recommended for more information on ways to control the microorganisms in the system.

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GLOSSARY OF TERMS

Different terms used in this study are:

Sugar: The crystals of sucrose (including any adherent molasses) recovered from the massecuite.

Molasses: The mother liquor separated from the crystals by centrifugling. It is termed first, second, third or final or A, B and C molasses.

Sugars: This term is used to describe sucrose plus invert of the solution.

Invert: Glucose and fructose contents of the solution.

Salts: Strictly speaking these are ionized compounds of the solution. In this study this term is used to describe both ionic materials as well as all other non-sugars (whether organic or inorganic) of the solution.

Brix: This represents the percentage of total dissolved matter in a sugar solution determined from the refractive index (RI). The brix of an impure solution is invariably higher than the solids obtained by drying because the nonsugars generally present are of higher RI than the sucrose. (Bx).

Pol: The "apparent" sucrose as determined by direct or single polarization of a specified weight of the solution.

Purity: 100 times ratio of sucrose and the brix.

Purity = 100 x sucrose/brix x 100

SMB: Simulated Moving Bed Chromatographic system.

Feed: This term is used for any material to be tested or separated that is introduced to the chromatographic columns either for pulse testing or for continuous experiments.

Products: Material coming out of the SMB plant resulting from the chromatographic separation.

Extract: It is a product of SMB system which is high in sugars and low in salts. (Extr.)

Raffinate: It is a product of SMB system which is high in salts, and low in sugars. (Raff.)

Eluent: Liquid (or gaseous) material used to desorb the components from the resin in the chromatographic column. Deionized water was used as eluent in this study.

NOMENCLATURE

A	column cross-sectional area, cm^2
A_i, B_j	coefficients for low concentration single feed
A_j, B_i	coefficients for binary or multicomponent feed
c	concentration of liquid, g/ml
HETP	height equivalent to a theoretical plate
K	distribution co-efficient
K_{i0}, K_{j0}	coefficient for low concentration single feed
L_T	total length of column, cm
L_E	effective length of column, cm
L_f	length of feed "plug", cm
m_f	feed mass, g
t	time, min
t'	retention time (mean time), min
q	concentration in solid phase, g/ml solid phase
Q	flow rate, ml/min.
U	velocity, cm/min
v	velocity of component in the SMB system, cm/min
v_{fluid}	interstitial velocity of fluid in the system
v_{solid}	solid velocity, cm/min
V'	retention volume of component
z	spatial interval, cm
ϵ	void volume
ρ	liquid density, g/cm^3
σ^2	variance

Subscripts:

F	fructose
G	glucose
i	for component 1
j	for component 2

APPENDIX A

Appendix A1

SMB Continuous Experiment Run #1
Clarified & Filtered Cane-Molasses
40.5 Brix

History of Experiment

Date	Phase	Flow Rates# Feed/Water/Ext./Rec. ml/min	Switch Time min.	Phase Time hrs	Cumulitive Run Time hrs	Remarks
3/26/91	I	20/120/30/218	8.6	02.33	02.33	(1)
3/26/91	II	20/130/30/218	8.6	01.00	03.33	(2)
3/26/91	II	20/124/30/218	8.6	03.22	06.55	(3)
3/26/91	IV	20/124/30/197	8.6	01.68	08.23	(4)
3/26/91	V	20/124/30/150	8.6	00.93	09.16	(5)

\# Raffinate by difference = 20 +120 -30 = 110 ml/min

(1) Stopped to increase water flow rate (120 to 130 ml/min)

(2) Stopped to decrease water flow rate (130 to 124 ml/min)

(3) Stopped to decreased recycle flow rate (to 197 ml/min)

(4) Stopped to decreased recycle flow rate (to 150 ml/min)

(5) Stopped the experiment as no improvement was observed.

Appendix A2

SMB Continuous Experiment Run #2
Clarified & Filtered Cane-Molasses
40.5 Brix

History of Experiment

Date	Phase	Flow Rates# Feed/Water/Ext./Rec. ml/min	Switch Time min	Phase Time hrs	Cumulitive Run Time hrs	Remarks
4/24/91	I	20/120/30/218	8.6	03.81	03.81	(1)
	II	20/120/30/218	8.9	01.56	05.37	(2)
	III	20/120/30/218	8.3	01.54	06.91	(3)
4/25/91	IV	20/120/30/250	8.6	04.29	11.20	(4)

\# Raffinate flow rate by difference = 20 +120 - 30 = 110 ml/min

(1) Stopped to increase switch time to 8.9 min.

(2) Stopped to decrease switch time to 8.3 min.

(3) Overnight break. Switch time changed to 8.6 min. and Recycle flow rate increased to 250 ml/min.

(4) Experiment finally stopped as no improved was observed.

Appendix A3

SMB Continuous Experiment Run #3
Clarified & Filtered Cane-Molasses
40.5 Brix

History of Experiment

Date	Phase	Flow Rates' Feed/Water/Ext./Rec. ml/min	Switch Time min	Phase Time hrs	Cumulitive Run Time hrs	Remarks
6/4/91	I	20/120/30/50	18	4.23	4.23	(1)
6/4/91	II	20/120/30/60	18	0.96	5.19	(2)
6/5/91	III	20/120/30/60	18	2.66	7.85	(3)
6/5/91	IV	20/120/30/70	18	0.65	8.50	(4)
6/5/91	V	00/120/30/70	18	0.61	9.11	(5)

Raffinate flow rate by difference = 20 + 120- 30 = 110 ml/min.

(1) Stopped to increase recycle flow rate to 60 ml/min.

(2) Stopped for overnight break.

(3) Stopped to increase recycle flow rate to 70 ml/min.

(4) Stopped to run without feed to correct the situation.

(5) Finaly stopped the experiment as no improvement was observed.

Appendix A4

SMB Continuous Experiment Run #4
Clarified & Filtered Cane Molasses
40.5 Brix

History of Experiment

Date	Phase	Flow Rates# Feed/Water/Ext./Rec. ml/min	Switch Time min	Phase Time hrs	Cumulitive Run Time hrs	Remarkss
6/6/91	I	20/120/30/250	8.6	5.02	5.02	(1)
6/7/91	II	20/120/30/250	8.6	2.14	7.16	(2)
6/7/91	III	20/120/30/250	8.6	1.29	8.45	(3)
6/8/91	IV	20/120/30/265	8.6	2.82	11.27	(4)
6/8/91	V	20/120/30/280	8.6	1.97	13.24	(5)
6/8/91	VI	20/120/30/280	8.6	11.67	24.91	(6)

\# Raffinate flow rate by difference = 20 +120 -30 = 110 ml/min.

(1) Stopped for overnight break.

(2) Stopped to change feed.

(3) Stopped to increase recycle flow rate to 265 ml/min.

(4) Stopped for overnight break.

(5) Started with recycle flow rate @ 280 ml/min. Stopped for lunch break.

(6) Stopped finally as there was no more feed.

Appendix A5

SMB Continuous Experiment Run #5
Clarified Cane-Molasses
41 Brix

History of Experiment

Date	Phase	Flow Rates# Feed/Water/Ext/Rec ml/min	Switch Time min.	Phase Time hrs	Cumulative Run Time hrs	Remarks
9/23/91	I	20/120/30/280	8.6	2.45	2.45	(1)
9/24/91	II	20/120/30/250	8.6	5.32	7.77	(2)
9/24/91	III	20/120/30/280	8.6	1.77	9.47	(3)
9/25/91	IV	20/120/30/280	8.6	6.73	16.20	(4)
9/26/91	V	20/120/30/280	8.6	2.40	18.60	(5)
9/26/91	VI	20/120/30/290	8.6	4.70	23.30	(6)
9/27/91	VII	20/120/30/290	8.6	0.10	23.40	(7)
9/27/91	VIII	20/120/30/290	8.6	0.55	23.95	(8)
9/27/91	IX	20/120/30/290	8.6	1.78	25.73	(9)
9/28/91	X	20/120/30/280	8.6	1.15	26.88	(10)
9/28/91	XI	20/120/30/280	8.6	0.62	27.50	(11)
9/28/91	XII	20/120/30/280	8.6	3.10	30.60	(12)
9/29/91	XIII	20/120/30/280	8.6	0.15	30.75	(13)
9/29/91	XIV	20/120/30/280	8.6	1.73	32.48	(14)
9/30/91	XV	20/120/30/280	8.6	0.77	33.25	(15)
9/30/91	XVI	20/120/30/290	8.6	0	34.85	(16)
9/30/91	XVII	20/120/30/290	8.6	1.86	36.71	(17)

\# Raffinate flow rate by difference= 20+120-30 = 110 ml/min

(1) Stopped for overnight break.

(2) Started with reduced recycle flow rate i.e. 250 ml/min. At 5.32 hrs increased recycle flow rate to 280 ml/min without stopping the experiment

(3) Stopped for overnight break.

(4) Stopped for overnight break.

(5) At 18.60 hrs Recycle flow rate was increased to 290 ml/min without stopping experiment.

...contd Appendix A5

(6) Stopped for overnight break.

(7) Stopped for computer program problem.

(8) Stopped as column #4 was dried up. Column #4 backwashed.

(9) Stopped for overnight break. Column #8 backwashed.

(10) Recycle flow rate decreased to 280 ml/min. Stopped for low purity of extract. Column #1 backwashed.

(11) Stopped for leakage at bottom pipe of Column #5.

(12) Stopped for overnight break. Column #1 backwashed.

(13) Stopped after 8.6 min for computer program problem.

(14) Stopped for overnight break. Column #6 backwashed.

(15) At 33.25 hrs Recycle flow rate increased to 290 ml/min without stopping experiment.

(16) At 34.85 hrs stopped for low purity. Checked concentration distribution curve.

(17) Stopped the experiment.

Appendix A6

SMB Continuous Experiment Run #6
Clarified & Filtered Cane-Molasses
60.5 Brix

History of Experiment

Date	Phase	Flow Rates# Feed/Water/Ext./Rec. ml/min	Switch Time min	Phase Time hrs	Cumulative Run Time hrs	Remarks
12/9/91	I	20/120/30/280	8.6	4.48	4.48	(1)
12/9/91	II	20/120/30/280	8.6	0.52	5.00	(2)
12/10/91	III	20/120/30/280	8.6	0.84	5.86	(3)
12/10/91	IV	20/120/30/280	8.6	5.16	11.00	(4)
12/11/91	V	20/120/30/280	8.6	0.38	11.38	(5)
12/11/91	VI	20/120/30/280	8.6	0.02	11.40	(6)
12/11/91	VII	20/120/30/280	8.6	0.46	11.86	(7)
12/11/91	VIII	20/120/30/280	8.6	1.38	13.24	(8)
12/11/91	IX	20/120/30/280	8.6	1.77	15.01	(9)
12/12/91	X	20/120/30/280	8.6	0.045	15.095	(10)
12/12/91	XI	20/120/30/280	8.6	0.070	15.129	(11)
12/12/91	XII	20/120/30/280	8.6	2.172	17.300	(12)
12/12/91	XIII	20/120/30/280	8.6	0.028	17.328	(13)
12/12/91	XIV	20/120/30/280	8.6	3.798	21.126	(14)
12/13/91	XV	20/120/30/280	8.6	7.456	28.582	(15)

Raffinate flow rate by difference = 20 + 120 - 30 = 110 ml/min.

(1) Stopped for problem at Column #7 (leakage)

(2) Stopped for overnight break.

(3) Stopped for flow rate check-up.

(4) Stopped for purity drop for pressure limits on pumps/overnight break.

(5) Stopped for problem with column #3 (drying).

(6) Stopped for problem with column #1 (drying).

(7) Stopped for problem with column #1 (drying).

(8) Stopped for problem with column #1 (dried-up). Column #1 back-washed.

...contd Appendix A6

(9) Stopped for overnight break.

(10) Stopped for water flow rate check-up.

(11) Stopped for column #1 leaked from top.

(12) Stopped for column #8 leaked from top.

(13) Stopped fro column #8 leaked from top.

(14) Stopped for overnight break.

(15) Stopped finally the experiment.

APPENDIX B

Appendix B1

Run #1 HPLC Analysis

Extract

Sample	Time, hrs	Salts %	Sucrose %	Invert %	Sugars %
S101	0.50	100.00	0.00	0.00	0.00
S102	1.50	8.74	69.98	20.35	91.26
S103	2.50	1.04	80.99	17.07	98.96
S104	3.50	20.01	66.10	8.96	79.99
S105	4.50	42.08	48.19	8.36	57.92
S106	5.50	43.04	46.34	9.05	56.96
S107	6.50	47.35	41.06	10.52	52.65
S108	7.50	50.47	38.14	9.33	49.53
S109	8.50	52.41	39.15	5.99	47.59

Run #1 HPLC Analysis

Raffinate

Sample	Time, hrs	Salts %	Sucrose %	Invert %	Sugars %
NS101	0.50	100.00	0.00	0.00	0.00
NS102	0.75	100.00	0.00	0.00	0.00
NS103	1.25	100.00	0.00	0.00	0.00
NS104	1.75	100.00	0.00	0.00	0.00
NS105	2.25	83.55	16.45	0.00	16.45
NS106	2.75	43.81	36.35	19.84	56.19
NS107	3.25	43.85	35.87	20.27	56.15
NS108	3.75	32.41	67.59	0.00	67.59
NS109	4.25	16.95	61.15	20.86	83.05
NS110	4.75	20.29	67.37	12.34	79.71
NS111	5.25	18.20	59.52	18.36	81.80
NS112	5.75				
NS113	6.25	15.10	64.55	20.34	84.90
NS114	6.75				

Appendix B2

Run #2 HPLC Analysis
Extract

Sample	Time,hrs	Suc. %	Invert %	Salts %	Sugars %
S201	0.50	33.32	66.53	0.00	100.00
S202	1.50	78.16	21.83	0.00	100.00
S203	2.50	83.62	12.41	2.07	97.93
S210	3.40	77.40	5.12	12.60	87.40
S204	4.31	81.71	10.71	5.33	94.67
S211	5.09	79.22	14.97	3.86	96.14
S205	5.87	83.35	14.79	1.86	98.14
S212	6.63	74.92	7.14	14.17	85.83
S206	7.40	80.88	11.77	5.07	94.93
S207	8.40	79.77	12.30	4.89	95.11
S208	9.40	78.78	8.12	10.31	89.69
S209	10.40	76.01	8.05	13.11	86.89
S213	11.05	70.88	8.81	17.07	82.93

Run #2 HPLC Analysis
Raffinate

Sample	Time,hrs	Suc. %	Invert %	Salts %	Sugars %
NS201	0.25	0.00	0.00	0.00	0.00
NS202	0.75	0.00	0.00	0.00	0.00
NS203	1.25	0.00	0.00	0.00	0.00
NS204	1.75	0.00	0.00	0.00	0.00
NS205	2.25	22.87	69.79	0.00	100.00
NS206	2.75	16.49	69.99	13.51	86.49
NS219	3.25	23.11	31.55	45.33	54.67
NS220	3.65	30.85	26.93	42.22	57.78
NS207	4.06	14.71	14.78	70.51	29.49
NS208	4.56	11.84	7.77	80.39	19.61
NS221	5.09	16.94	11.68	71.38	28.62
NS209	5.62	19.78	8.27	71.94	28.06
NS210	6.12	12.36	16.28	71.35	28.65
NS222	6.66	26.37	38.38	35.24	64.76
NS211	7.15	8.87	14.81	76.31	23.69
NS212	7.65	13.12	12.72	74.15	25.85
NS213	8.15	10.09	19.45	70.45	29.55
NS214	8.65	8.47	14.51	77.01	22.99
NS215	9.15	12.42	21.53	66.04	33.96
NS216	9.65	19.85	17.76	62.39	37.61
NS217	10.24	16.65	19.46	63.88	36.12
NS218	10.74	21.78	19.38	58.83	41.17
NS223	11.05	20.99	20.75	58.25	41.75

Appendix B3

Run #3 HPLC Analysis
Extract

Sample	Time,hrs	Salts %	Suc. %	Invert %	Sugars %
S301	0.50	100.00	0.00	0.00	0.00
S302	1.50	25.46	19.48	55.06	74.54
S303	2.50	3.16	59.20	37.65	96.84
S304	3.50	2.91	86.40	10.68	97.09
S305	4.12	0.84	76.56	12.11	99.16
S306	5.73	4.95	75.00	12.96	95.05
S307	6.68	2.07	79.52	18.41	97.93
S308	6.68	1.88	77.98	18.16	98.12
S309	7.31	4.15	79.48	13.18	95.85
S310	8.17	15.01	69.48	10.53	84.99
S311	8.80	15.00	67.51	15.37	85.00

Run #3 HPLC Analysis

Raffinate

Sample	Time,hrs	Salts %	Suc. %	Invert %	Sugars %
NS301	0.25	100.00	0.00	0.00	0.00
NS303	1.25	79.35	0.00	20.63	20.65
NS305	2.25	92.02	7.98	0.00	7.98
NS307	3.25	67.47	23.83	8.70	32.53
NS309	4.12	79.43	1.60	18.97	20.57
NS311	4.95	79.69	2.14	18.17	20.31
NS313	5.94	77.69	3.28	15.79	22.31
NS315	6.94	68.97	1.49	28.94	31.03
NS317	7.77	68.22	2.62	28.63	31.78
NS319	8.42	74.57	2.97	21.60	25.43

Appendix B4

RUN #04 HPLC Analysis

Extract

Sample	Time hrs	Salts %	Suc. %	Invert %	Sugars %
S201	1.00	33.89	38.97	27.13	66.11
S202	2.00	9.91	30.17	55.90	90.09
S203	3.00	4.77	63.45	31.77	95.23
S204	4.00	0.00	86.45	13.55	100.00
S205	4.75	0.00	88.41	11.59	100.00
S206	5.52	0.00	88.33	11.67	100.00
S207	6.52	0.00	83.60	15.42	100.00
S208	7.65	2.32	80.77	11.64	97.68
S209	8.95	3.11	81.73	13.68	96.89
S210	9.95	1.12	81.67	14.89	98.88
S211	10.81	2.52	81.74	12.59	97.48
S212	11.72	7.15	71.13	19.33	92.85
S213	12.41	2.73	76.07	16.04	97.27
S214	13.14	4.52	73.98	15.46	95.48
S215	13.61	2.48	79.58	14.55	97.52
S216	14.49	2.24	80.96	14.60	97.76
S217	15.99	2.57	75.72	20.58	97.43
S218	17.99	8.36	78.82	12.81	91.64
S219	19.99	4.43	80.77	14.80	95.57
S220	21.49	1.99	82.48	15.53	98.01
S221	22.49	1.57	82.93	15.49	98.43
S222	23.49	2.54	81.51	15.95	97.46
S223	24.44	2.04	85.08	12.88	97.96

...contd Appendix B4

Run #4 HPLC ANALYSIS

Raffinate

Prod. #	Time hrs	Salts %	Suc. %	Invert %	Sugars %
NS201	0.25	92.66	7.34	0.00	7.34
NS203	1.25	97.56	0.00	2.44	2.44
NS207	3.25	90.99	0.00	9.00	9.01
NS209	4.25	73.23	1.18	25.58	26.77
NS211	5.26	76.17	2.16	21.67	23.83
NS213	6.27	74.72	5.10	20.18	25.28
NS215	7.41	65.52	9.80	24.66	34.48
NS217	8.30	69.02	13.57	17.40	30.98
NS219	9.58	72.93	11.96	15.11	27.07
NS221	10.70	71.76	10.86	17.38	28.24
NS223	12.02	75.75	6.26	17.99	24.25
NS225	13.00	66.60	4.40	19.01	33.40
NS229	15.49	83.93	2.90	13.17	16.07
NS231	16.49	75.50	2.73	21.76	24.50
NS233	17.49	76.60	3.10	20.30	23.40
NS235	18.49	71.29	3.47	25.24	28.71
NS237	19.49	71.94	5.12	22.94	28.06
NS239	20.49	74.78	4.59	18.10	25.22
NS241	21.49	72.05	3.58	21.13	27.95
NS243	22.49	65.35	6.30	21.51	34.65
NS245	23.49	71.08	4.41	22.45	28.92
NS247	24.49	64.58	5.92	28.27	35.42

Appendix B5

RUN #5 HPLC Analysis

Extract

Sample	Time hrs	Salts %	Suc. %	Invert %	Sugars %
S501	0.79				
S502	0.93				
S503	1.08				
S504	1.36	0.65	23.12	76.08	99.35
S508	2.82	12.88	31.07	56.05	87.12
S510	3.24	2.41	88.86	8.74	97.60
S513	3.82	2.66	86.55	10.79	97.34
S517	4.38	3.45	85.51	11.03	96.55
S518	4.53	3.35	86.42	10.23	96.65
S519	4.68	3.43	84.85	11.72	96.57
S521	4.96	3.65	86.30	10.05	96.35
S523	5.25	3.70	84.81	11.50	96.31
S525	5.53	4.98	82.44	12.59	95.02
S529	6.11	5.34	81.02	13.64	94.66
S531	6.39	5.40	82.76	11.84	94.60
S533	6.68	6.07	82.80	11.13	93.93
S535	6.97	7.08	81.02	11.90	92.92
S537	7.25	8.56	79.41	12.04	91.45
S539	7.54	7.83	80.59	11.58	92.17
S541	7.83	9.14	80.40	10.47	90.87
S543	8.11	8.23	79.74	12.03	91.77
S545	8.40	7.04	78.37	14.59	92.96
S547	8.68	5.31	80.87	13.82	94.69
S549	8.97	5.77	80.71	13.52	94.23
S552	9.40	1.05	84.20	14.75	98.95
S554	9.83	1.22	82.86	15.92	98.78
S556	10.12	0.91	84.46	14.63	99.09
S558	10.41	0.72	82.07	17.22	99.29
S560	10.70	0.86	83.13	16.01	99.14
S562	10.98	0.78	82.30	16.92	99.22
S564	11.27	0.66	84.76	14.59	99.34
S566	11.56	0.88	86.49	12.63	99.12
S568	11.84	6.49	80.59	12.93	93.52
S570	12.12	8.04	80.61	11.35	91.96
S572	12.42	5.49	81.80	12.71	94.51
S574	12.70	1.09	89.63	9.29	98.91
S576	12.99	1.33	89.68	8.99	98.67
S578	13.27	1.30	89.22	9.49	98.70
S580	13.56	1.17	89.56	9.27	98.83

...contd Appendix B5

Extract

Sample	Time hrs	Salts %	Suc. %	Invert %	Sugars %
S582	13.85	2.96	87.22	9.82	97.04
S584	14.13	0.89	85.99	13.12	99.11
S588	14.71	1.11	86.83	12.15	98.89
S590	15.00	1.03	84.41	14.56	98.97
S592	15.29	1.10	83.80	15.10	98.90
S596	15.85	1.01	85.04	13.94	98.99
S598	16.13	0.99	84.78	14.23	99.01
S599	16.28	7.04	83.48	9.48	92.96
S600	16.42	7.30	79.40	12.30	92.70
S603	16.86	7.17	77.67	15.16	92.83
S606	17.28	1.99	79.55	18.46	98.02
S609	17.72	3.68	80.77	15.59	96.35
S612	18.14	4.35	78.01	17.65	95.66
S615	18.72	4.58	85.40	10.02	95.42
S618	19.15	3.71	85.77	10.52	96.29
S621	19.57	6.48	84.29	9.22	93.52
S624	20.01	5.38	85.56	9.06	94.62
S627	20.44	5.34	84.37	10.29	94.67
S630	20.87	8.67	78.52	12.82	91.33
S632	21.16	6.27	83.42	10.31	93.73
S636	21.73	8.76	81.38	9.86	91.24
S639	22.32	9.71	77.17	13.12	90.29
S641	22.59	8.57	77.83	13.51	91.43
S644	23.03	10.43	76.82	12.77	89.57
S646	23.56	8.56	75.83	15.61	91.44
S648	24.10	13.79	73.91	12.30	86.21
S650	24.68	16.87	71.35	11.78	83.13
S651	24.96	11.56	77.38	11.06	88.44
S652	25.26	6.90	79.35	13.75	93.10
S654	25.71	6.02	81.70	12.28	93.98
S655	25.97	10.17	81.64	8.18	89.83
S656	26.27	11.47	75.18	13.35	88.53
S657	26.53	26.35	64.54	9.12	73.65
S658	26.82	28.53	60.70	10.78	71.47
S659	26.98	11.61	72.85	15.54	88.39
S660	27.10	8.39	79.97	11.65	91.61
S662	27.39	5.01	86.01	8.98	94.99
S664	27.68	4.34	81.27	14.39	95.66
S665	27.82	5.57	79.24	15.20	94.43
S666	28.11	6.57	78.82	16.61	93.43
S667	28.26	5.84	81.19	12.97	94.16
S668	28.40	4.59	80.25	15.16	95.41

...contd Appendix B5

Extract

Sample	Time hrs	Salts %	Suc. %	Invert %	Sugars %
S670	28.68	3.33	83.38	13.29	96.67
S672	28.96	4.75	82.58	12.67	95.25
S674	29.24	7.14	81.19	11.67	92.86
S676	29.54	5.66	82.31	12.04	94.35
S679	29.96	3.57	85.27	11.17	96.43
S683	30.54	6.70	81.80	11.50	93.31
S685	30.93	16.32	69.82	13.86	83.68
S687	31.22	15.07	77.30	7.64	84.93
S689	31.50	9.27	79.56	11.17	90.73
S693	32.08	10.48	75.33	14.18	89.52
S694	32.73	8.19	77.55	14.26	91.81
S696	32.98	8.48	78.71	12.81	91.52
S698	33.28	6.22	79.10	14.69	93.78
S700	33.57	9.35	77.45	13.20	90.65
S702	33.85	17.87	71.33	10.80	82.13
S704	34.13	16.22	73.45	10.33	83.78
S706	34.43	15.39	75.86	8.75	84.61
S708	34.71	11.59	78.39	10.02	88.41
S711	35.21	6.11	81.67	12.23	93.89
S713	35.50	5.84	84.55	9.62	94.16
S715	35.81	7.41	80.67	11.92	92.59
S717	36.08	14.77	71.22	14.01	85.23
S719	36.36	18.52	70.65	10.83	81.48
S721	36.64	16.52	71.38	12.10	83.48

Raffinate

Sample	Time hrs	Salts %	Suc. %	Invert %	Sugars %
NS503	1.78	87.56	8.82	3.62	12.44
NS504	2.08	60.10	29.69	10.21	39.90
NS505	2.37	91.46	7.82	0.72	8.54
NS507	2.82	15.82	26.37	57.81	84.18
NS510	3.39	21.82	21.36	56.82	78.18
NS512	3.82	59.33	12.57	28.10	40.67
NS515	4.24	22.93	21.13	55.95	77.07
NS519	4.82	42.55	39.43	18.02	57.45
NS526	5.82	28.78	48.12	23.10	71.22
NS533	6.82	33.84	45.61	21.00	66.16
NS540	7.83	25.21	51.99	22.80	74.79

...contd Appendix B5

RUN #5 HPLC Analysis

Raffinate

Sample	Time hrs	Salts %	Suc. %	Invert %	Sugars %
NS547	8.82	64.43	23.68	[illegible]	35.57
NS554	9.98	[illegible]	16.07	[illegible]	28.22
NS561	10.99	[illegible]	[illegible]	18.32	32.29
NS568	[illegible]	59.78	18.60	[illegible]	40.25
NS575	13.00	56.16	25.99	17.86	43.84
NS581	13.86	[illegible]	29.30	13.09	42.39
NS590	15.15	63.40	25.39	[illegible]	36.60
NS597	16.15	60.24	25.61	14.16	39.76
NS598	16.28	64.43	[illegible]	13.86	35.57
NS599	16.42	68.59	18.05	13.37	31.41
NS602	16.85	[illegible]	14.33	[illegible]	31.75
NS610	18.00	46.94	28.86	24.20	53.06
NS611	18.14	42.40	29.56	28.04	57.60
NS616	19.00	48.02	24.00	27.99	51.98
NS623	20.00	56.10	25.23	18.67	43.90
NS630	21.00	50.64	24.02	25.34	49.36
NS637	22.00	41.54	39.23	19.23	58.46
NS643	23.03	43.92	39.34	16.75	56.08
NS645	23.56	30.52	41.16	28.33	69.48
NS650	24.31	54.69	24.19	[illegible]	45.31
NS653	25.06	76.38	14.07	9.54	23.62
NS654	25.69	[illegible]	32.93	55.95	88.79
NS657	26.55	32.18	43.74	23.08	67.82
NS659	27.73	30.59	7.41	62.01	69.41
NS661	28.02	75.88	17.82	6.30	24.12
NS668	28.54	75.29	15.52	9.19	24.71
NS673	29.25	70.47	12.52	17.01	29.53
NS675	29.68	68.21	11.26	20.35	31.79
NS681	30.55	71.89	11.30	16.81	28.11
NS683	31.06	62.84	22.06	15.10	37.16
NS690	32.07	49.85	30.93	19.22	50.15
NS692	32.85	91.43	6.25	2.31	8.57
NS695	33.28	58.13	17.67	24.15	41.87
NS698	33.70	67.53	14.51	17.96	32.47
NS705	34.71	48.88	31.12	20.00	51.12
NS709	35.64	59.53	24.77	15.70	40.47
NS716	36.64	46.86	31.35	21.79	53.14

Appendix B6

Run #6 HPLC analysis

Extract

Sample	Time hrs	Salts %	Suc. %	Invert %	Sugars %
S601	2.1	0.0	8.8	91.2	100.0
S602	2.4	0.0	7.6	92.4	100.0
S603	2.7	0.0	14.6	85.4	100.0
S604	3.0	0.0	14.1	85.9	100.0
S605	3.2	1.0	13.3	85.7	99.0
S606	3.7	2.4	35.4	62.1	97.6
S607	3.9	2.3	35.6	62.1	97.7
S608	4.2	1.9	37.7	60.4	98.1
S609	4.5	2.0	48.7	49.3	98.0
S610	4.8			0.0	0.0
S611	5.0	2.2	63.6	34.2	97.8
S612	5.2			0.0	0.0
S613	5.4	3.0	70.9	26.1	97.0
S614	5.8	2.7	77.2	20.2	97.3
S615	6.1	1.4	85.7	12.9	98.6
S616	6.4	1.5	84.2	14.3	98.5
S617	6.7	1.3	85.6	13.1	98.7
S618	7.0	1.1	86.3	12.5	98.9
S619	7.3	1.1	85.7	13.2	98.9
S620	7.5	1.7	86.5	11.8	98.3
S621	7.8	1.8	85.9	12.3	98.2
S622	8.1			0.0	0.0
S623	8.2	1.0	87.4	11.7	99.0
S624	8.7	1.6	84.5	11.9	96.4
S625	9.1	2.5	85.9	11.6	97.5
S626	9.5	7.5	80.4	12.1	92.5
S627	9.8	6.6	85.0	8.5	93.4
S628	10.1	6.6	82.2	11.3	93.4
S629	10.4	10.7	80.4	8.9	89.3
S630	10.7	12.1	78.1	9.8	87.9
S631	11.0	11.9	77.6	10.5	88.1
S632	11.2	20.1	62.8	17.1	79.9
S633	11.5	27.1	57.6	15.4	72.9
S634	11.8	28.7	55.3	16.0	71.3
S635	12.2	33.0	53.0	14.1	67.1
S636	12.6	30.9	56.6	12.5	69.1
S637	12.8	20.6	67.3	12.1	79.4
S638	13.1	15.1	71.8	13.1	84.9
S639	13.4	16.6	68.1	15.3	83.4
S640	13.7	12.1	73.0	14.9	87.9

...contd Appendix B6

Run #6 HPLC analysis

Extract

Sample	Time hrs	Salts %	Suc. %	Invert %	Sugars %
S641	14.0	16.0	68.8	15.2	84.0
S642	14.2	16.6	71.3	13.0	84.4
S643	14.5	10.5	74.8	14.7	89.5
S644	15.0	13.5	73.1	13.4	86.5
S645	15.4	9.3	75.5	15.1	90.7
S646	16.4	4.0	82.3	13.7	96.0
S647	17.5	6.6	79.5	14.0	93.4
S648	18.5	2.9	82.6	14.6	97.1
S620A	19.5	2.4	77.7	19.9	97.6
S621A	20.5	2.8	78.7	18.5	97.2
S649	21.8	2.9	85.1	12.0	97.1
S650	23.2	2.9	83.3	13.8	97.1
S651	24.1	2.5	83.4	14.1	97.5
S652	25.1	3.0	82.2	14.8	97.0
S653	26.2	3.4	81.3	15.2	96.6
S654	27.1	3.9	81.9	14.2	96.1
S655	27.7	5.1	82.2	12.7	94.9
S656	28.0	2.7	84.9	12.5	97.4
S657	28.6	2.3	85.8	11.9	97.7

...contd Appendix B6

Run #6 HPLC Analysis

Raffinate

Sample	Time hrs	Salts %	Suc. %	Invert %	Sugars %
NS601	2.1	100.0	0.0	0.0	0.0
NS602	2.4			0.0	0.0
NS603	2.7	98.1	1.3	0.6	1.9
NS604	3.0			0.0	0.0
NS605	3.2			0.0	0.0
NS606	3.7	89.2	2.6	8.3	10.9
NS607	3.9			0.0	0.0
NS608	4.2			0.0	0.0
NS609	4.5	74.7	2.5	22.8	25.3
NS610	4.8				
NS611	5.0			0.0	0.0
NS612	5.2				
NS613	5.4	66.4	2.7	30.9	33.6
NS614	5.8			0.0	0.0
NS615	6.1			0.0	0.0
NS616	6.4	72.0	3.1	24.9	28.0
NS617	6.7			0.0	0.0
NS618	7.0			0.0	0.0
NS619	7.3	76.4	2.8	20.8	23.6
NS620	7.5				
NS621	7.8			0.0	0.0
NS622	8.1				
NS623	8.2	63.0	3.3	33.7	37.0
NS624	8.7	65.5	3.8	30.7	34.5
NS625	9.1	54.5	6.2	39.4	45.6
NS626	9.5	52.3	8.8	38.8	47.7
NS627	9.8	58.5	8.6	32.9	41.5
NS628	10.1	52.1	12.8	35.2	47.9
NS629	10.4				
NS630	10.7				
NS631	11.0	47.0	23.1	30.0	53.0
NS632	11.2	51.7	19.5	28.8	48.3
NS633	11.5	38.5	32.8	28.8	61.6
NS634	11.8	6.9	34.4	58.7	93.1
NS635	12.2	21.1	38.7	40.2	78.9
NS636	12.6	47.4	25.6	27.0	52.6
NS637	12.8	42.4	36.9	20.8	57.7
NS638	13.1	39.4	39.1	21.5	60.6
NS639	13.4	74.7	22.3	3.0	25.3
NS640	13.7	49.2	13.2	37.6	50.8

...contd Appendix B6

Run #6 HPLC Analysis

Raffinate

Sample	Time hrs	Salts %	Suc. %	Invert %	Sugars %
NS641	14.0	60.6	16.2	23.3	39.4
NS642	14.2	61.9	16.3	21.8	38.1
NS643	14.5	53.0	19.4	27.6	47.0
NS644	15.0	60.2	14.8	25.0	39.8
NS646	16.4	70.3	7.1	22.6	29.7
NS647	17.5	68.9	4.5	26.6	31.1
NS648	18.5	72.7	9.6	17.7	27.3
NS637A	19.3	69.5	12.2	18.4	30.5
NS638A	19.8	65.0	13.7	21.2	35.0
NS639A	20.3	67.3	15.5	20.2	35.7
NS640A	20.8	64.2	11.7	24.2	35.8
NS641A	21.3	61.5	9.7	28.8	38.5
NS649	21.8	66.7	4.7	28.6	33.3
NS650	23.2	66.8	5.1	28.1	33.2
NS651	24.1	65.4	17.4	17.2	34.6
NS652	25.1	68.9	11.4	19.7	31.1
NS653	26.2	74.9	8.3	16.7	25.1
NS654	27.1	68.3	5.8	25.9	31.7
NS655	27.7	60.0	7.1	32.9	40.0
NS656	28.0	64.1	11.0	24.9	35.9
NS657	28.6	68.5	11.9	19.6	31.5

APPENDIX C

Appendix C1

Run #1: Material Balance

Table 1.1: Total Weight of Feed/Extract/Raffinate

Components	Feed	Extract	Raffinate
Total Weight, Kg	12.606	16.364	47.000
Brix	43.050	8.000	3.000
Total Solids, Kg	5.105	1.299	1.410

Table 1.2: Mass Balance

Components	Feed	Extract	Raffinate	On system	After Steady State
Solids, Kg	5.105	1.299	1.410	2.396	2.709
Sucrose, Kg	2.231	0.979	0.207	1.045	1.186
Invert, Kg	0.674	0.204	0.153	0.317	0.357
Nonsugars, Kg	2.200	0.116	1.050	1.034	1.166
Total Sugars, Kg	2.905	1.183	0.360	1.362	1.543

Table 1.3: % Recovery (Through SMB System)

Components	Extract	Raffinate
Sucrose	82.5	17.5
Invert	57.1	42.9
Nonsugars	10.0	90.0
Total Sugars	76.7	23.3

Appendix C2

Run #2: Material Balance

Table 2.1: Total Weight of Feed/Extract/Raffinate

Components	Feed	Extract	Raffinate
Total Weight, Kg	15.708	20.507	67.268
Brix	40.5	9.85	2.3
Total Solids, Kg	6.361	2.020	1.547

Table 2.2: Mass Balance

Components	Feed	Extract	Raffinate	On System	After Steady State
Solids, Kg	6.361	2.020	1.547	2.794	3.567
Sucrose,Kg	2.780	1.597	0.236	0.947	1.833
Invert, Kg	0.840	0.212	0.282	0.346	0.494
Nonsugars, Kg	2.740	0.211	1.029	1.500	1.240
Total Sugars, Kg	3.620	1.800	0.518	1.302	2.318

Table 2.3: % Recovery (through SMB System)

Components	Extract	Raffinate
Sucrose	87.1	12.9
Invert	42.9	57.1
Nonsugars	17.0	83.0
Total Sugars	77.7	22.3

Appendix C3

Run #3: Material Balance

Table 3.1: Total Weight of Feed/Extract/Raffinate

Components	Feed	Extract	Raffinate
Total Weight, Kg	12.341	16.364	57.010
Brix	40.5	7.94	0.78
Total Sloids, Kg	4.998	1.299	0.444

Table 3.2: Mass Balance

Components	Feed	Extract	Raffinate	On System	After Steady State
Solids, Kg	4.998	1.299	0.444	3.255	1.743
Sucrose, Kg	2.184	0.980	0.015	1.189	0.995
Invert, Kg	0.659	0.204	0.089	0.366	0.293
Nonsugars, Kg	2.154	0.115	0.340	1.699	0.455
Total Sugars, Kg	2.844	1.183	0.104	1.557	1.287

Table 3.3: % Recovery (Through SMB System)

Component	Extract	Raffinate
Sucrose	98.5	1.5
Invert	69.6	30.4
Nonsugars	25.3	74.7
Total Sugars	91.8	8.2

Appendix C4

Run #4: Material Balance

Table 4.1: Total Weight of Feed/Extract/Raffinate

Components	Feed	Extract	Raffinate
Total Weight, Kg	31.70 + 6.38 = 37.55	40.83	166.67
Brix	i) 40.5; ii) 48.0	13.88	4.11
Total Solids, Kg	12.62 + 3.04 = 15.66	5.67	6.85

Table 4.2: Mass Balance

Components	Feed	Extract	Raffinate	On System	After Steady State
Solids, Kg	15.66	5.67	6.85	3.14	12.52
Sucrose, Kg	6.84	4.59	0.72	1.53	5.31
Invert, Kg	2.07	0.85	0.77	0.45	1.62
Nonsugars, Kg	6.75	0.23	5.36	1.16	5.59
Total Sugars, Kg	8.91	5.44	1.49	1.98	6.93

Table 4.3: % Recovery (Through SMB System)

Components	Extract	Raffinate
Sucrose	86.5	13.5
Invert	52.5	47.5
Nonsugars	4.1	95.9
Total Sugars	78.5	21.5

Appendix C5

Run #5: Material Balance

Table 5.1: Total Weight of Feed/Extract/Raffinate

Components	Feed	Extract	Raffinate
Total Weight, Kg	58.239	63.34	227.59
Brix	41.00	14.50	4.50
Total Solids, Kg	23.88	9.18	10.24

Table 5.2: Mass Balance

Components	Feed	Extract	Raffinate	On System	After Steady State
Solids, Kg	23.88	9.18	10.24	4.16	19.42
Sucrose,Kg	12.22	7.42	2.38	2.27	9.80
Invert, Kg	3.46	1.09	1.80	0.53	2.89
Nonsugars, Kg	8.19	0.66	6.06	1.36	6.72
Total Sugars, Kg	15.69	8.51	4.18	2.80	12.69

Table 5.3: % Recovery (Through SMB System)

Components	Extract	Raffinate
Sucrose	75.7	24.3
Invert	37.7	62.3
Nonsugars	9.8	90.2
Total Sugars	67.1	32.9

Appendix C6

Run #6: Material Balance

Table 6.1: Total Weight of Feed/Extract/Raffinate

Components	Feed	Extract	Raffinate
Total Weight, Kg	51.166	51.830	176.61
Brix	60.5	21.84	6.1
Total Solids, Kg	30.955	11.321	10.770

Table 6.2: Mass Balance

Components	Feed	Extract	Raffinate	On System	After Steady State
Solids, Kg	30.955	11.321	10.770	8.904	2.209
Sucrose,Kg	15.468	9.091	1.235	5.143	10.325
Invert, Kg	6.541	1.755	2.665	2.121	4.420
Nonsugars, Kg	8.946	0.475	6.870	1.601	7.345
Total Sugars, Kg	21.009	10.846	3.900	7.264	13.745

Table 6.3: % Recovery (through SMB System)

Components	Extract	Raffinate
Sucrose	88.05	11.95
Invert	39.77	60.23
Nonsugars	6.46	93.57
Total Sugars	78.90	21.10

VITA

Khalid Iqbal was born in Sialkot District, Pakistan, on March 25, 1954. He received his high school education in Rahimyarkhan, Pakistan. He then attended Government College of Industrial Technology in Nawab Shah, Pakistan and obtained a Bachelor of Science degree in Industrial Technology in 1972. He then remained self-employed for about 6 years. Most of this time he worked on his family farm producing sugarcane as major crop. In 1978 he joined the Department of Applied Chemistry, University of Karachi, Pakistan and earned Bachelor of Science (Honours) and Master of Science degrees in 1980 and 1981 respectively. In 1981, he joined Fauji Foundation (Pakistan) Sugar Division and was working for its sugar mills before he arrived in the USA.

In 1988, he was selected by USAID for a scholarship for graduate studies at Louisiana State University. He joined Food Science Department, LSU in January 1989. He is presently a candidate for the Doctor of Philosophy degree in Food Science Department.

He is a member of Institute of Food Technologists, USA; American Society of Sugar Cane Technologists, Louisiana Division, and Pakistan Society of Sugar Technologists.

He is married to Zeenat and they are parents of two boys, Haroon and Osamah.

DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Khalid Iqbal

Major Field: Food Science

Title of Dissertation: Recovery of Sugars from Cane Molasses by Continuous Simulated Moving Bed Ion-Exclusion Chromatography.

Approved:

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February 20, 1992